Hydrogenation of Alkylaromatics over Rh/silica.

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Abstract

The hydrogenation, and competitive hydrogenation, of toluene, ethylbenzene, propylbenzene and the xylenes has been studied over a rhodium catalyst in the liquid phase at 323 K and 3 barg. The reactivity of the aromatics gave an order of para-xylene > ortho-xylene > meta-xylene > toluene > ethylbenzene >> propylbenzene. Kinetic analysis revealed that the order of reaction in hydrogen was typically first order while the reaction order in toluene was zero order and negative half order for ethylbenzene. The reaction order for propylbenzene and the xylenes was negative first order. Apparent activation energies were calculated and all were in the range 26-46 $kJ.mol^{-1}$. Competitive hydrogenation between toluene, ethylbenzene and propylbenzene revealed that the propylbenzene was the most strongly adsorbed aromatic in agreement with the strongly negative reaction order. The xylenes gave an order of reactivity of *para* > *ortho* > *meta* following the increasing negative reaction order. Reactions with deuterium revealed an inverse kinetic isotope effect, most likely related to the change in hybridization of the carbon from sp^2 to sp^3, for all reactions, except that of *ortho*-xylene. Rapid exchange of the methyl group hydrogens was observed with all the xylenes, whereas total exchange was noted with toluene. The generation of trans-1,2-dimethylcyclohexane was explained by the formation of two intermediates, 1,2-dimethylcyclohexene and 1,6-dimethylcyclohexene, which give the cis-1,2-dimethylcyclohexane and trans-1,2-dimethylcyclohexane respectively.

Introduction

Hydrogenation technology in chemicals production is ubiquitous. It has often been considered mature technology with little scope for new developments: an area that is not fashionable. However, this belies the difficulties and unknowns that are still extant in hydrogenation. In 1905, Sabatier and Senderence [1] reported the first catalytic hydrogenation of benzene. They 'attacked' the benzene ring with hydrogen at atmospheric pressure and temperatures between 343 K and 473 K over a nickel catalyst and succeeded in converting it to cyclohexane [1]. This was the first example of hydrogenation of an aromatic ring. Nowadays aromatic hydrogenation is a major industrial process with around 4.6 mT of benzene hydrogenated to cyclohexane each year.

The catalytic hydrogenation of alkylbenzenes to saturated cyclic products is also an important reaction although it does not get the same interest. It is used in lowering the aromatic content in diesel fuels for environmental reasons [2]. Much of the aromatic content in fuels comes from Pyrolysis gasoline (PyGas), which is a by-product of high temperature naphtha cracking to produce ethylene and propylene. It is a mixture of highly unsaturated hydrocarbons and contains considerable amounts of aromatics, normally 40-80% (benzene, toluene and xylene), together with paraffins, olefins and diolefins. The composition depends on the feedstock and operating conditions and hence varies from plant to plant. With an aromatic content of around 65 wt % pygas has been used as a gasoline blend due to its high octane number [3]. However with new legalisation set to lower the aromatic content in gasoline [4] further hydrogenation of the aromatics especially as a mixture will be required.

The hydrogenation of alkylbenzenes has only been subject to limited study and even that is focused on toluene and the xylenes [5-10]. To find studies of ethylbenzene or propylbenzene hydrogenation we must go back to 1945 [11]. Although there is a more recent study on ethylbenzene hydrogenation [12] examining the kinetics in the gas phase, no other literature on propylbenzene could be found. The xylenes, which have been examined slightly more extensively, are still poorly considered [5-10] compared to the hydrogenation of benzene, which has been the subject of numerous studies [13].

The hydrogenation of alkylbenzenes is affected by the length and position of the substituent on the benzene ring [5,6,11]. In general the rate of hydrogenation decreases as the length of the substituent increases, while for the xylenes the *para*- isomer has been found to be the most active [5,6,9]. Toppineen *et al.*[14,15] investigated in detail the hydrogenation of five aromatics (di- and tri-substituted alkyl benzenes, xylenes, mesitylene, and *p*-cymene) over Ni/Al_2O_3. They also concluded that the reaction rate is affected by the number, length and position of the substituent. They found that the hydrogenation rate increased as the number of substituents decreased (mesitylene < xylenes < toluene < benzene) and the reaction rate was found to increase as the length of substituent decreased (cumene < ethylbenzene < toluene < benzene). For the xylenes they also found the *para*-isomer to be the most reactive.

Many of the kinetic studies have been gas phase studies at moderate temperatures [8,9], while the early work in the liquid phase did not undertake any kinetic analysis. Also there is a dearth of information on rhodium as the active phase, with no study examining the xylenes or ethyl- or propylbenzene [5,16]. In this study we have undertaken a basic kinetic analysis of the hydrogenation of toluene, ethylbenzene, propylbenzene and the xylenes over a rhodium

catalyst at low temperatures, examined the competitive hydrogenation and probed the mechanism of exchange and hydrogenation using deuterium and deuterated toluene.

Experimental

The catalyst used throughout this study was a 2.5 % Rh/silica supplied by Johnson Matthey (code: M01074). The silica support was supplied by Davison Catalysts and the catalysts, which were supplied and characterised by Johnson Matthey, were prepared using an incipient-wetness method using aqueous rhodium chloride salts. The catalysts were dried overnight at 333 K and reduced in flowing hydrogen at 473 K for 2 hours before being cooled and exposed to air. The surface area (311 m^2g^{-1}) and pore size (13.9 nm) were measured using standard BET methodology, while metal surface area (4.7 m^2g^{-1}, dispersion 43 %; average metal crystallite size 2.6 nm) was measured by hydrogen chemisorption with reproducibility of ±0.5 m^2g^{-1} (all characterisation data supplied by Johnson Matthey).

The hydrogenation reactions were performed in a 500 cm^3 Büchi autoclave stirred tank reactor supplied with an oil heating jacket. The temperature was measured in the liquid slurry with accuracy of ± 0.1 K and controlled by a high temperature oil circulator to ± 0.5 K. The reactor was equipped with a variable speed stirrer connected to a magnetic drive that could be controlled to ± 5 rpm. The pressure and gas flow was controlled by a Büchi press-flow gas controller with an accuracy of ± 0.01 barg and measurement of the consumed hydrogen to 0.1 mmol. The gas controller was used to achieve a constant hydrogen pressure in the autoclave. The reactions were performed as follows, in a typical hydrogenation experiment catalyst (100 mg) was charged to the autoclave with 320 ml of isopropanol (IPA) and heated to the reduction temperature under slow stirring (300 rpm). *In-situ* reduction of

the catalyst was performed at 343 K by sparging hydrogen gas at a flow rate of 280 cm^3 min^{-1} through the mixture for 0.5 h while stirring at 300 rpm. After the reduction process was completed, the stirrer was turned off and the reactor was purged with nitrogen twice and pressurized to 1 barg pressure. The gas controller was used to measure the flow of hydrogen, deuterium or inert gas to the reactor and also to measure the hydrogen/deuterium consumed in the reaction. The contents of the reactor were then heated to the desired reaction temperature under slow stirring. After reaching the desired temperature (303 – 333 K) the stirrer was turned off and 1.0 cm^3 of toluene (Fischer, 99 % 9.42 mmol), d_8-toluene (Sigma-Aldrich, 99 % D, 9.43 mmol) ethylbenzene (Sigma-Aldrich, 99.5 % 8.17 mmol), propylbenzene (Sigma-Aldrich, 98 % 7.18 mmol), ortho-xylene (Sigma-Aldrich, 99 %, 8.30 mmol), meta-xylene Sigma-Aldrich, 99 %, 8.11mmol) or para-xylene (Sigma-Aldrich, 99 %, 8.12 mmol) in 10 ml of isopropanol was added into the reactor vessel through the reactor inlet to give a total reaction volume of 330 ml. The solution was stirred at 1000 rpm to allow for mixing. The stirrer was then turned off and the reactor pressurised with N_2 to 1 barg before a sample was withdrawn (2.5 ml). The reactor was de-pressurised, before being purged twice with hydrogen then pressurised with hydrogen to the desired reaction pressure (1 – 5 barg). Once the vessel was pressurised the reaction was started by switching the stirrer on at 1000 rpm: this was taken as the zero time of the reaction. The progress of the reaction was followed by withdrawing samples of 2.5 cm^3 at different time intervals during the reaction. The moles of hydrogen consumed during the reaction were also monitored and recorded. Mass balance was 100±5 %. Liquid samples were analysed using a Thermo Finnigan Focus GC equipped with an AS 3000 autosampler. The column used was an HP-1701, 30 m x 0.25 mm x 1µm film thickness. GC-MS of the selected samples were performed on a Shimadzu GC-2010 equipped with an AOC-20i auto-injector unit and an GCMS-OP2010S detector. The column was either a Zebron ZB-5MS 30 m × 0.25 mm ×

0.25 µm film thickness used only for the analysis of the reaction intermediates or a Petrocol^{TM} Supleco Analytical fused silica capillary column of 100 m × 0.25 mm × 0.5 µm film thickness. The detected reaction intermediates mass spectrograms were compared in the Nist05.lib using Lib2Nist v1.0.23.

D-NMR were performed on a Bruker 500 Ultra Shield-NMR system using a custom pulse and acquisition AU-programme provided by the Bruker company using the Deuterium-lock channel as the data channel.

Results

Detailed reaction profiles, determination of rate constants, activation energy plots, order of reaction plots and analysis are all reported in the Supplementary Information. The summary data is presented in the paper along with key results.

Single substrate hydrogenation

The hydrogenation of toluene, ethylbenzene, propylbenzene, ortho-xylene, meta-xylene and para-xylene was carried out as outlined in the experimental section. The effect of temperature (303 K – 343 K), hydrogen pressure (2 – 5 barg) and aromatic concentration (3.6 mmol. – 11.1 mmol.) was investigated to determine apparent activation energies and orders of reaction. The data is summarised in table 1.

The hydrogenation of toluene, ethylbenzene and propylbenzene resulted in the formation of a single product, the cyclohexyl derivative. A small quantity of the relevant cyclohexene (< 2 %) was formed during the reaction as an intermediate. However the xylenes formed cis- and

Table 1. Summary of kinetic parameters.

Compound	Ea (kJ.mol^{-1})	order in H_2	Order in organic	k^a (min^{-1}, x10^{-3})
Toluene	31±0	1.1±0.3	0.1±0.3	18.3±0.4
Ethylbenzene	46±7	1.1±0.3	-0.4±0.1	12.4±0.6
Propylbenzene	39±2	1.0±0.0	-0.8±0.1	3.3±0.1
Ortho-xylene	25±5	0.8±0.3	-0.7±0.0	22.3±0.4
Meta-xylene	27±3	0.7±0.3	-0.9±0.2	18.3±0.8
Para-xylene	42±3	1.1±0.1	-0.6±0.1	23.4±0.6

(a) k, first order rate constant measured at 323 K, 3 barg and ~8 mmol reactant

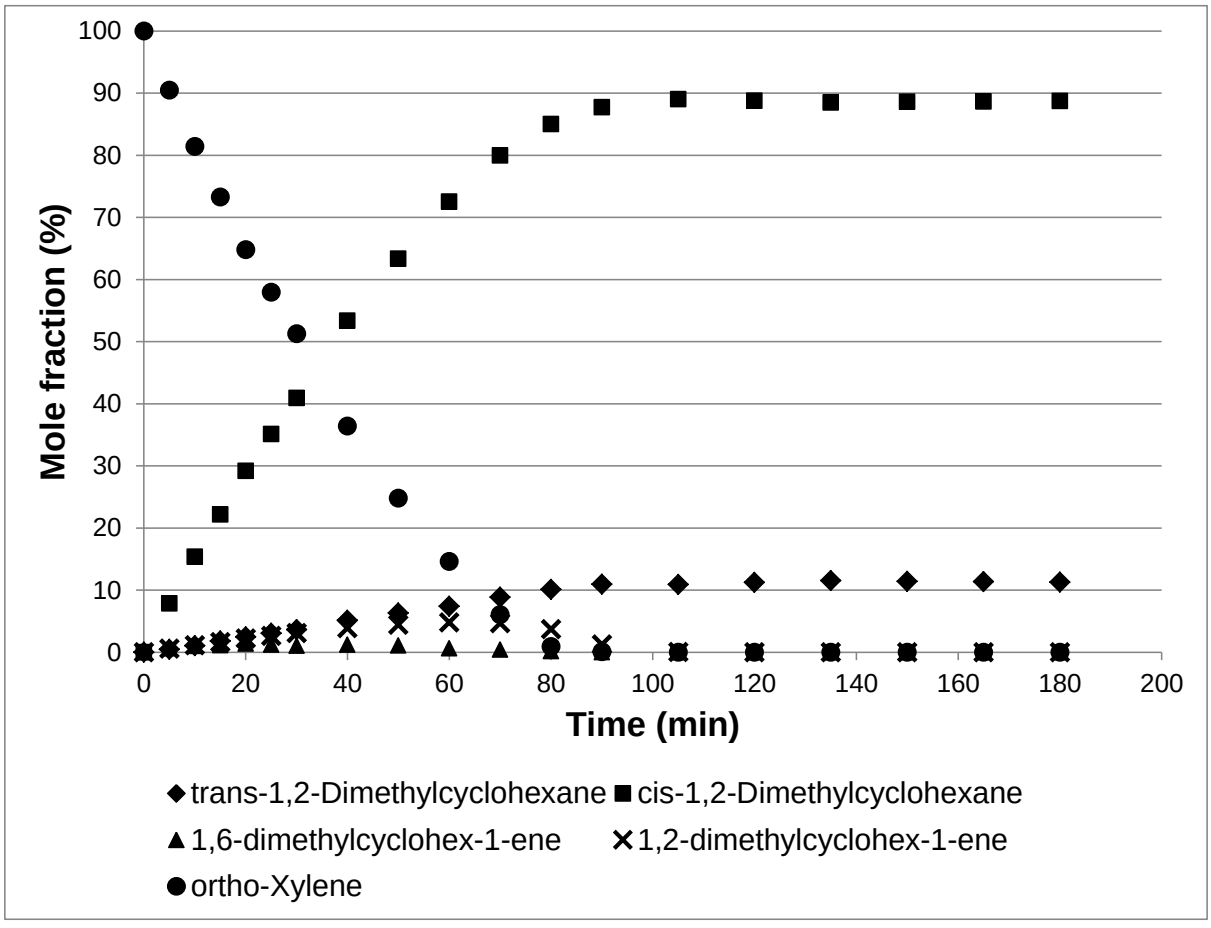


Figure 1. Hydrogenation of ortho-xylene (323 K, 3 barg, ~8 mmol).

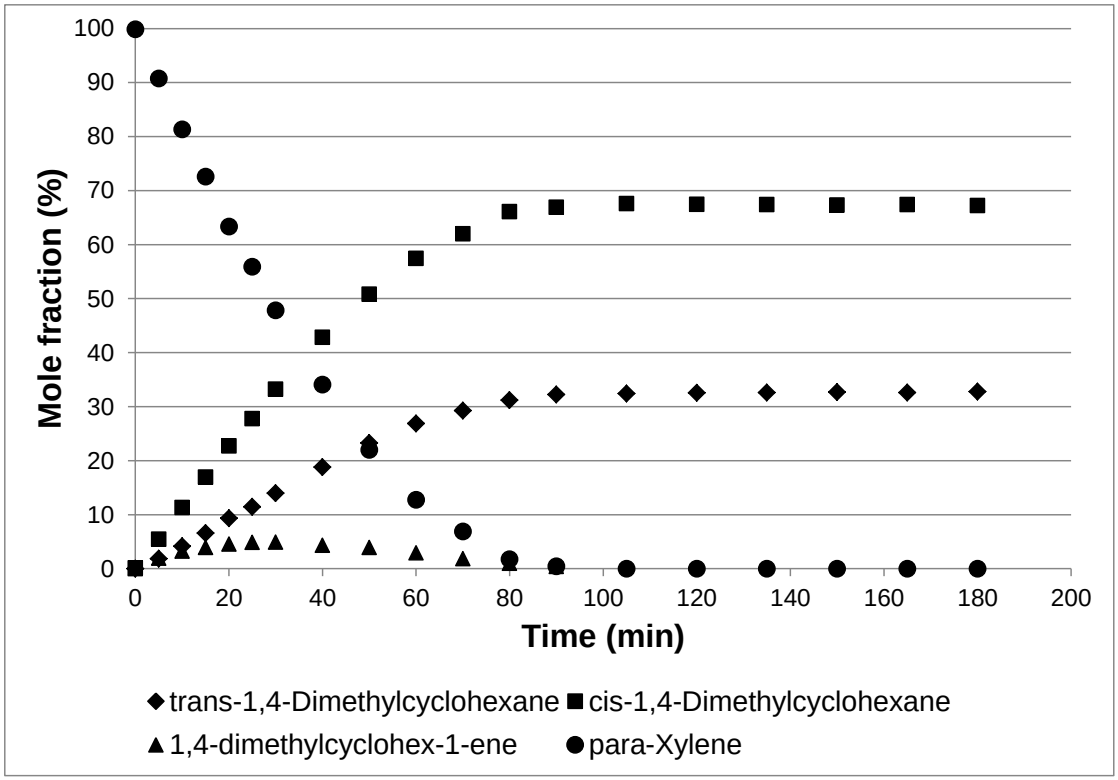


Figure 2. Hydrogenation of para-xylene (323 K, 3 barg, ~8 mmol).

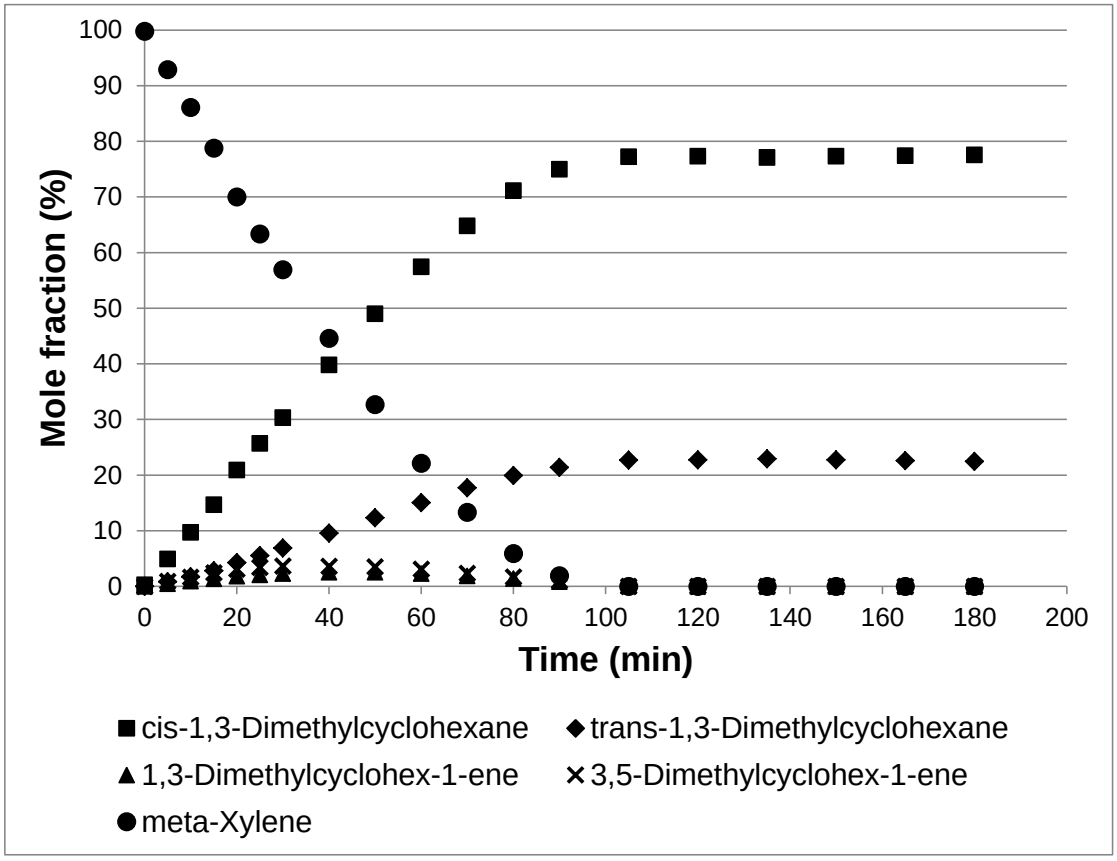


Figure 3. Hydrogenation of meta-xylene (323 K, 3 barg, ~8 mmol).

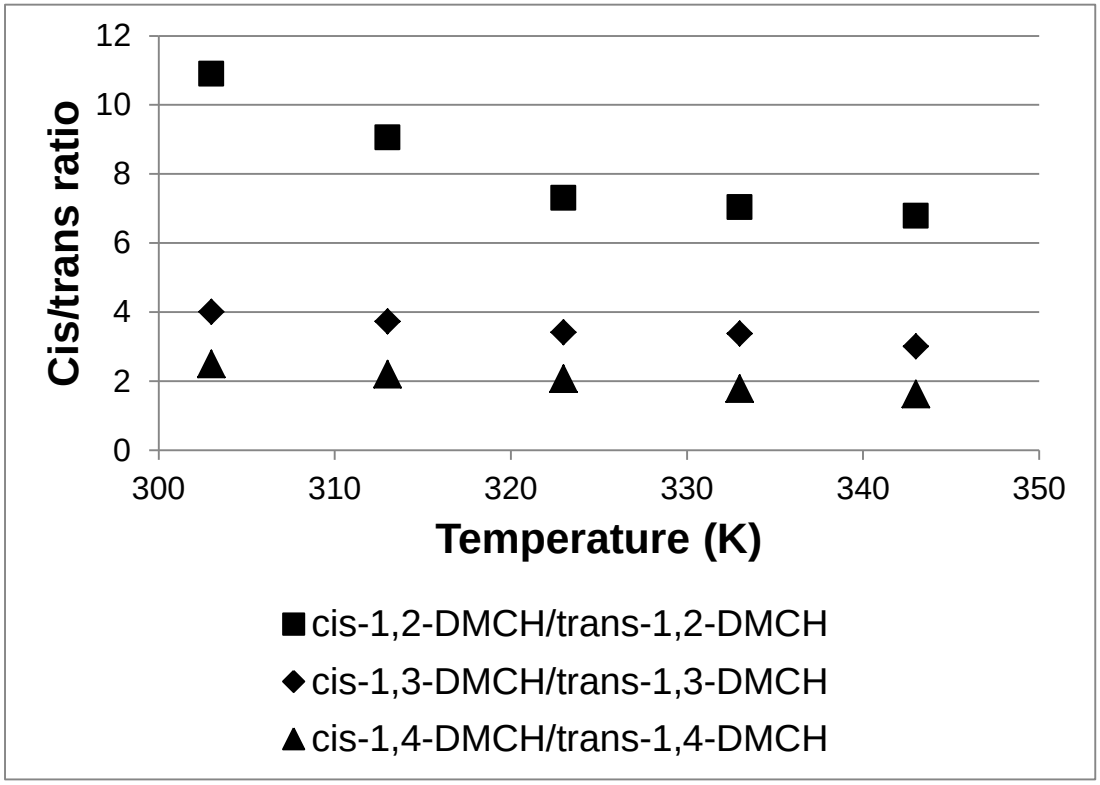


Figure 4. Change of cis/trans ratio with temperature (3 barg, ~8 mmol). DMCH = dimethylcyclohexane. 1,2-DMCH is formed from *ortho*-xylene, 1,3-DMCH is formed from *meta*-xylene and 1,4-DMCH is formed from *para*-xylene.

trans-dimethylcyclohexyl isomers with intermediate dimethylcyclohexenyls. A reaction profile for each xylene isomer is shown in figures 1- 3. At 323 K the cis:trans ratio of the dialkylcyclohexanes at 100 % xylene conversion was 8.1:1 for ortho-xylene, 3.5:1 for meta-xylene and 2.1:1 for para-xylene. The effect of temperature on cis/trans ratio is shown in figure 4. Hydrogen pressure and xylene concentration had no effect on the cis/trans ratio.

Competitive reactions.

The competitive hydrogenations of toluene, ethylbenzene and propylbenzene were investigated. The compounds were tested in pairs and also with all three reactants. Figure 5

shows the conversion with time for the alkylbenzenes as single reactants and when hydrogenated together. The first order rate constants are reported in table 2. A similar process was carried out for the xylenes and the first order rate constants are reported in table 3. Due to an overlap between cis-1,4-dimethylcyclohexane and trans-1,3-dimethylcyclohexane cis:trans ratios for meta- and para-xylene were not obtained when both were present however ratios were obtained for ortho-xylene products and are reported in table 4.

Table 2. Competitive hydrogenation of alkylbenzenes at 323 K, 3 barg and 8 mmol.

Reactant	First order rate constant, k (min^{-1}, $x10^{-3}$)			
	Toluene/EB[a]	Toluene/PB[b]	EB/PB	Toluene/EB/PB
Toluene	21.2±0.6	7.2±0.2		4.3±0.1
Ethylbenzene	16.9±0.5		4.5±0.1	2.9±0.1
Propylbenzene		7.3±0.1	5.4±0.1	4.2±0.1

a) EB, ethylbenzene
b) PB, propylbenzene

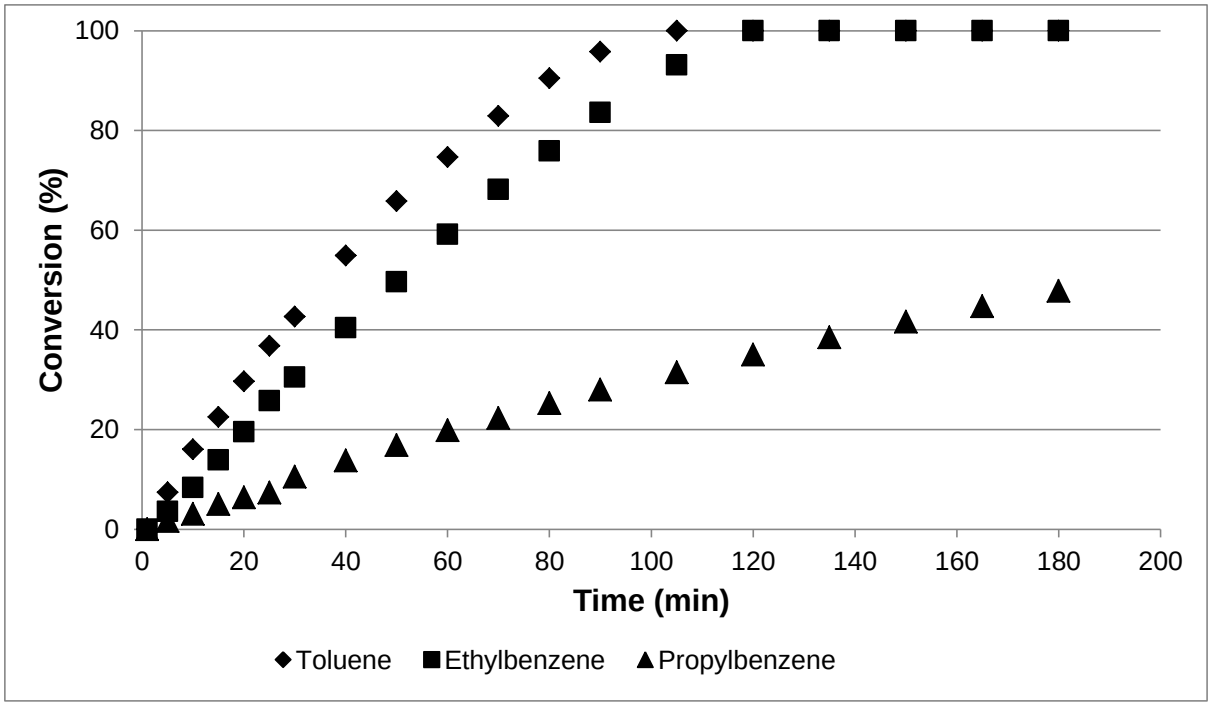
Table 3. Competitive hydrogenation of xylenes at 323 K, 3 barg and 8 mmol.

Reactant	First order rate constant, k (min^{-1}, $x10^{-3}$)			
	Ortho/meta	Ortho/para	Meta/para	Ortho/meta/para
Ortho-xylene	5.0±0.1	7.9±0.1		5.4±0.1
Meta-xylene	1.9±0.0		5.0±0.1	1.6±0.0
Para-xylene		3.3±0.1	6.3±0.1	2.5±0.0

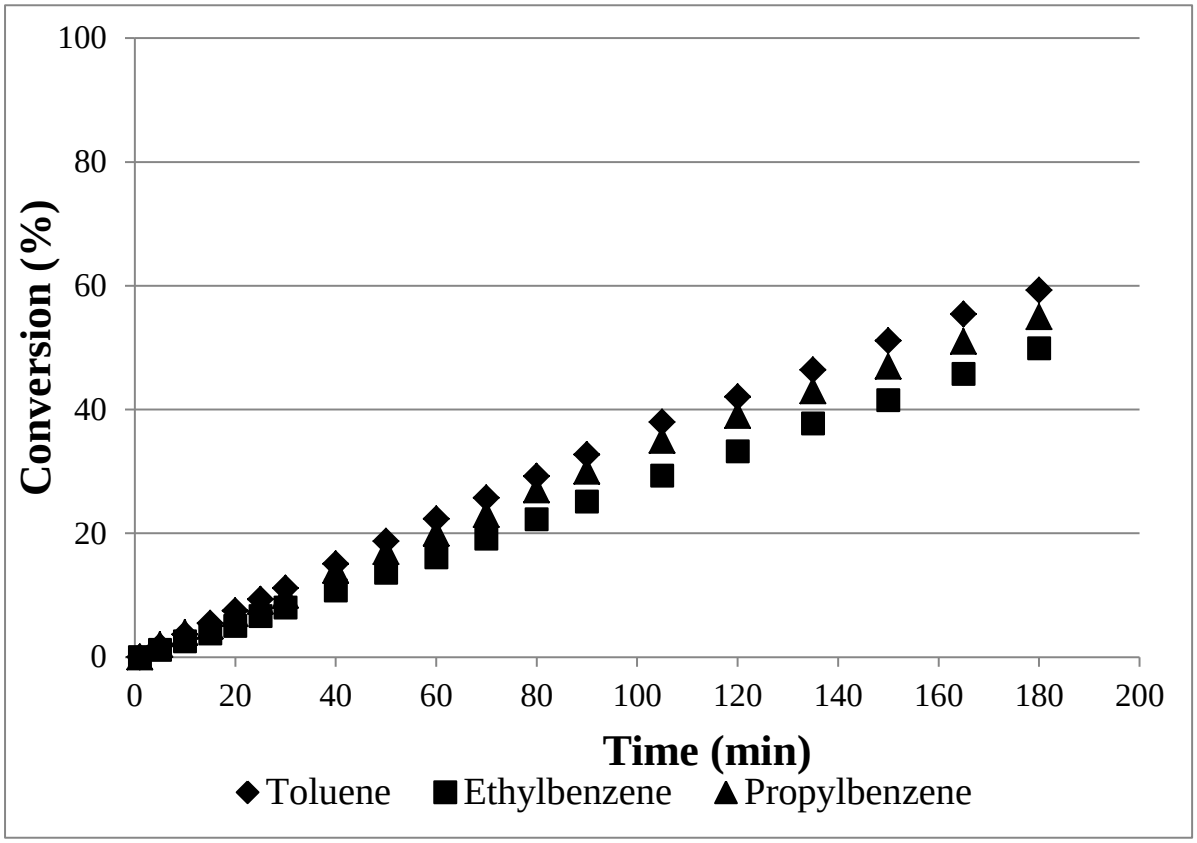
Table 4. Ratio of cis-1,2-dimethylcyclohexane and trans-1,2-dimethylcyclohexane during competitive hydrogenation (60 % conversion of ortho-xylene, 323 K and 3 barg).

	Ortho-xylene	Ortho/meta	Ortho/para	Ortho/meta/para
Cis/trans ratio	10.4	17.5	15.3	16.9
		3.9[a]	2.4[b]	

a) cis:trans ratio for 1,3-dimethylcyclohexanes at 60 % meta-xylene conversion
b) cis:trans ratio for 1,4-dimethylcyclohexanes at 60 % para-xylene conversion



a) conversion of the alkylbenzenes as single reactants



b) conversion of the alkylbenzenes hydrogenated together

Figure 5. Hydrogenation of the alkylbenzenes a) individually and b) as a 1:1:1 mixture.

Conditions: 3 barg hydrogen, 323 K, ~8 mmol alkylbenzene.

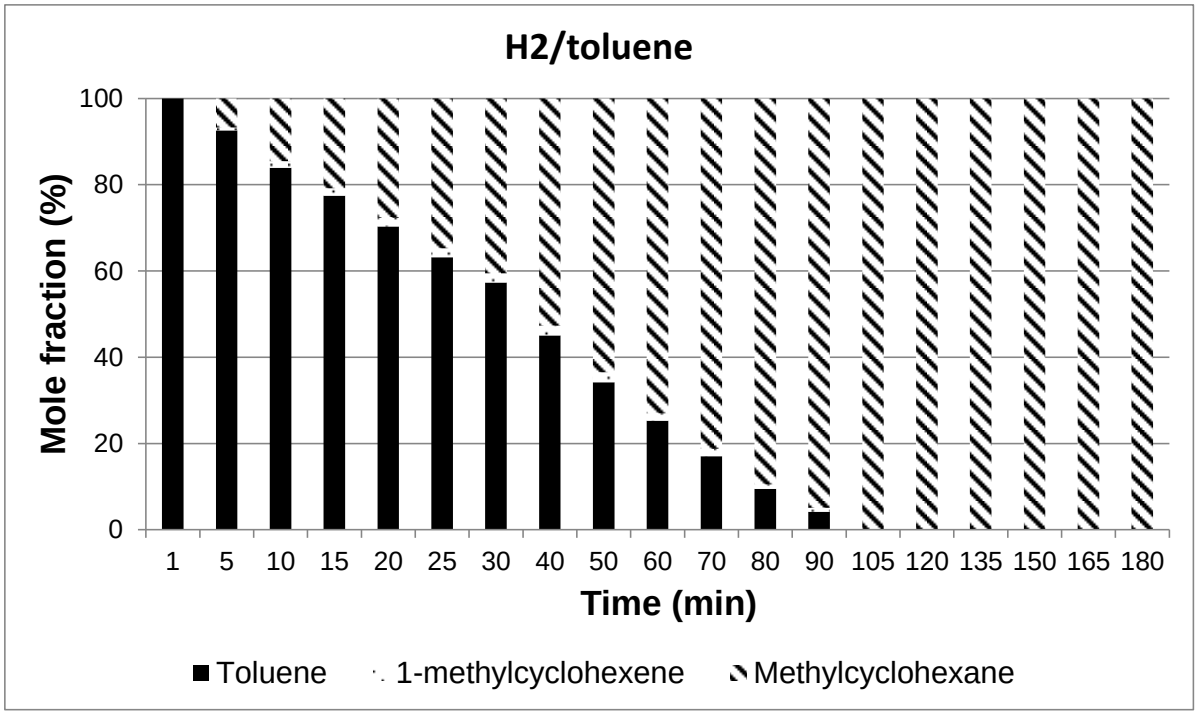
Deuterium reactions

Reactions were performed using deuterium rather than hydrogen for the reduction and the hydrogenation. Experiments were also performed using d_8-toluene with hydrogen and deuterium. The first order rate constants for the hydrogen and deuterium reactions are reported in table 5. Apart from ortho-xylene, all the reactants register an inverse kinetic isotope effect.

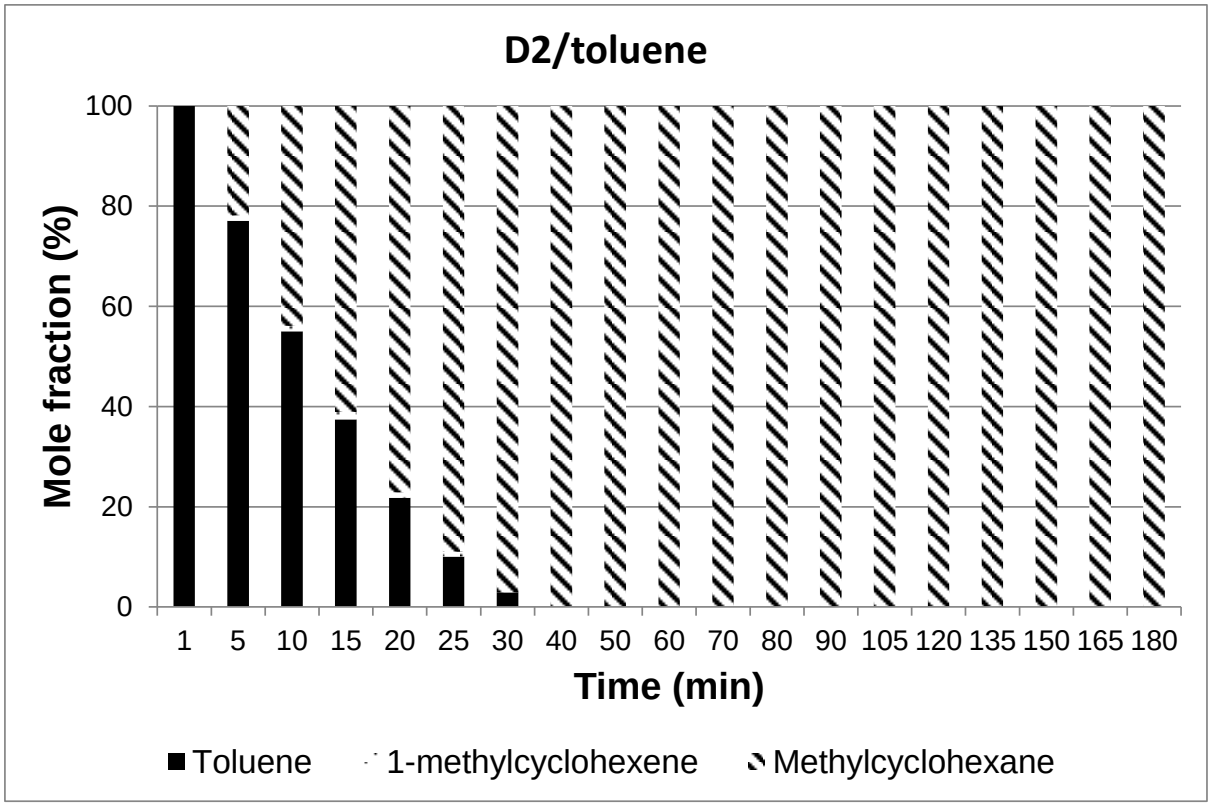
Table 5. 1st order rate constants for hydrogenation and deuteration.

	Reactant					
	toluene	EB	PB	o-xylene	m-xylene	p-xylene
k_H (min^{-1}, $x10^{-3}$)	18.3±0.4	12.4±0.6	3.3±0.1	22.3±0.4	18.3±0.8	23.4±0.6
k_D (min^{-1}, $x10^{-3}$)	65.6±0.4	32.9±1.4	12.5±0.0	19.0±0.4	23.6±0.1	61.8±3.3
k_H/k_D	0.28	0.38	0.26	1.17	0.78	0.38

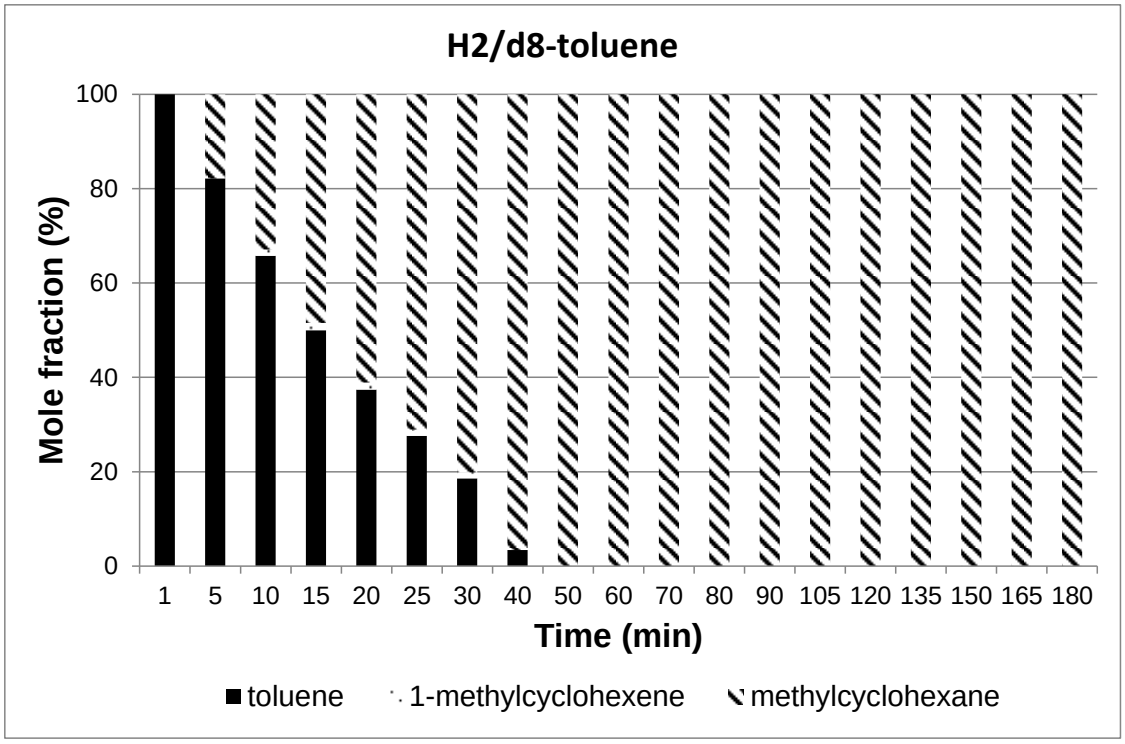
The toluene system was further examined using d_8-toluene with hydrogen and deuterium. Figure 6 shows the reaction profiles of four reactions; a) toluene hydrogenation under hydrogen pressure ($k = 18.8x10^{-3}$ min^{-1}), b) toluene hydrogenation under deuterium ($k = 65.6x10^{-3}$ min^{-1}), c) d_8-toluene hydrogenation under hydrogen ($k = 55.0x10^{-3}$ min^{-1}) and d) deuterated-toluene hydrogenation under deuterium ($k = 67.4x10^{-3}$ min^{-1}). Clearly reactions involving deuterium and deuterated-toluene, i.e. reactions (b), (c) and (d) were faster than reaction (a), which was the protiated form.



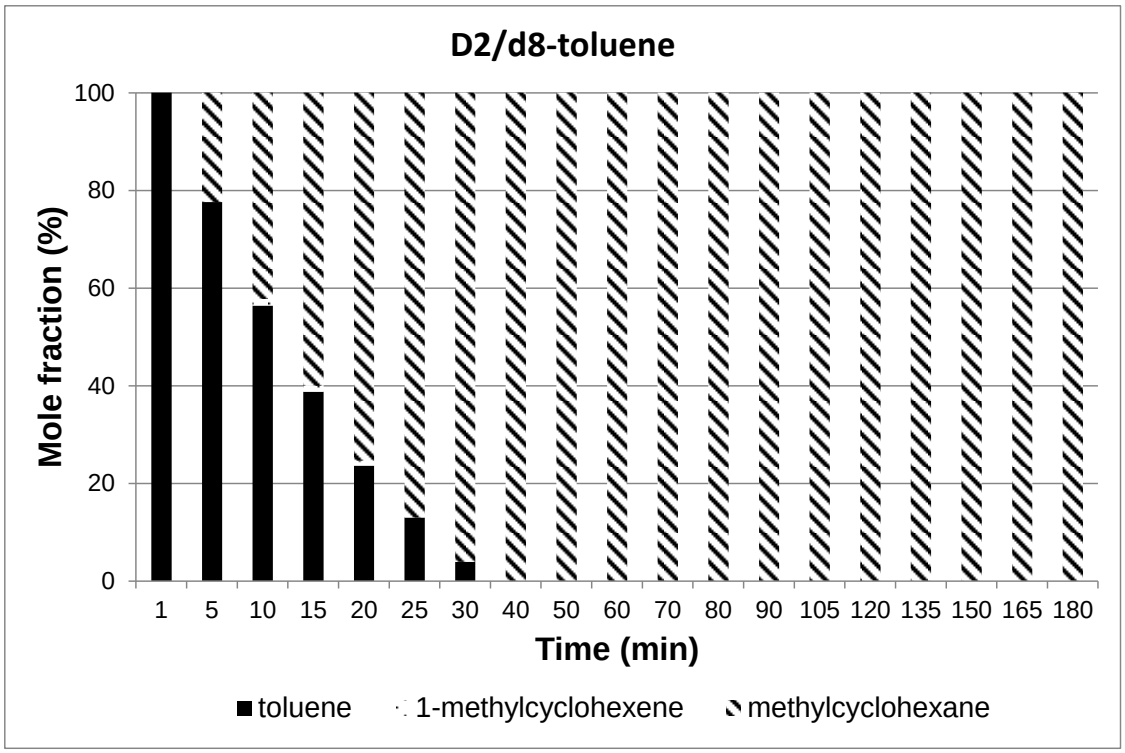
a) hydrogenation of toluene with hydrogen



b) hydrogenation of toluene with deuterium



c) hydrogenation of d_8-toulene with hydrogen



d) hydrogenation of d_8-toluene with deuterium

Figure 6. Reaction profiles for a) hydrogenation of toluene with hydrogen, b) hydrogenation of toluene with deuterium, c) hydrogenation of d_8-toulene with hydrogen and d) hydrogenation of d_8-toluene with deuterium. Conditions: 323 K, 3 barg, ~8 mmol.

A number of samples were collected from toluene and deuterated-toluene reactions with deuterium and hydrogen to be analysed by NMR. One sample was taken at the start of the toluene/deuterium reaction. Another sample was taken from the reaction of deuterated-toluene with hydrogen after 10 min. A reference sample of deuterated-toluene was also run (not shown). The spectra are shown in Figures 7 and 8.

The xylenes were also hydrogenated using deuterium and the products analysed by D-NMR and GC-MS. Both D-NMR and GC-MS analysis confirmed incorporation of deuterium in the methyl groups but not the aromatic ring prior to hydrogenation for all the xylenes. The ratio of the deuterium incorporation into the xylenes is shown in Figure 9.

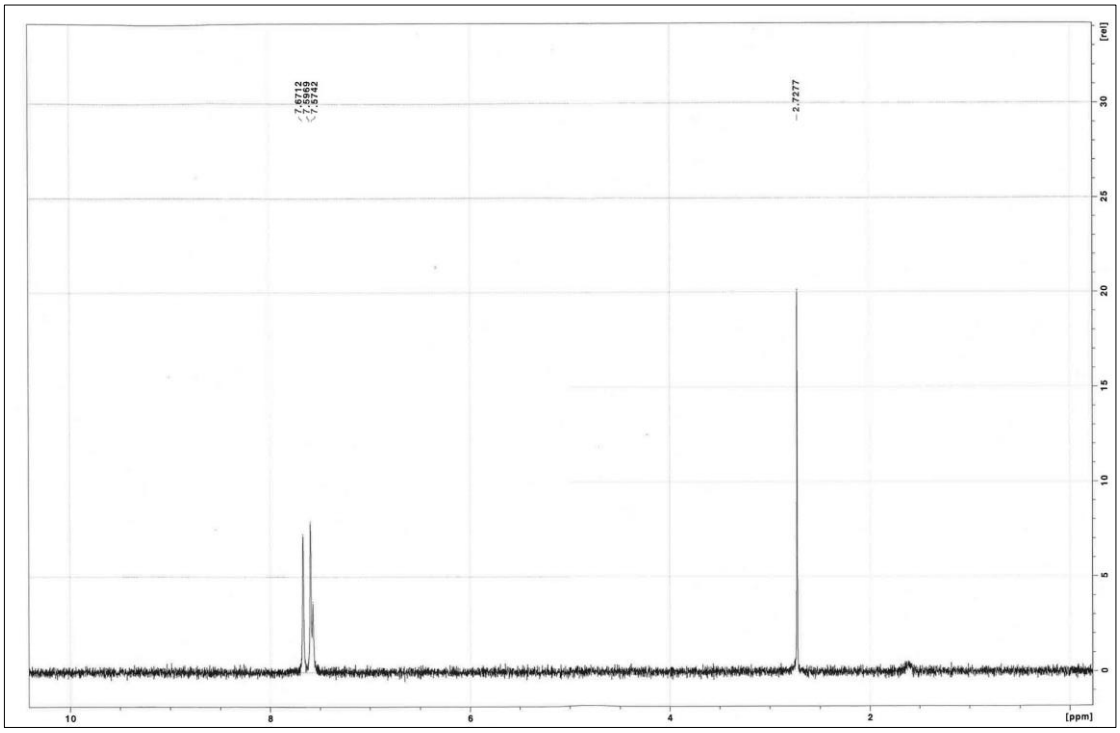


Figure 7. D-NMR spectrum of toluene hydrogenation with D_2 at t = 0 min.

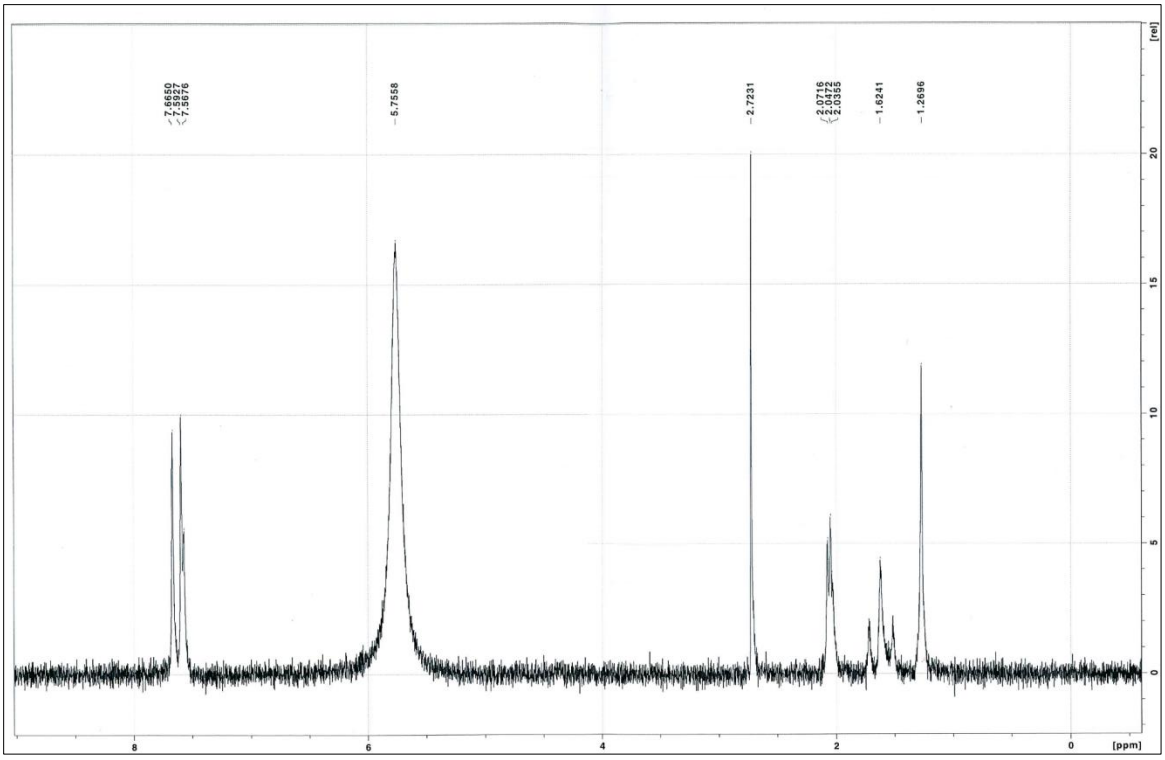


Figure 8. D-NMR spectrum of d_8-toluene hydrogenation with $H_2$1 at t = 10 min.

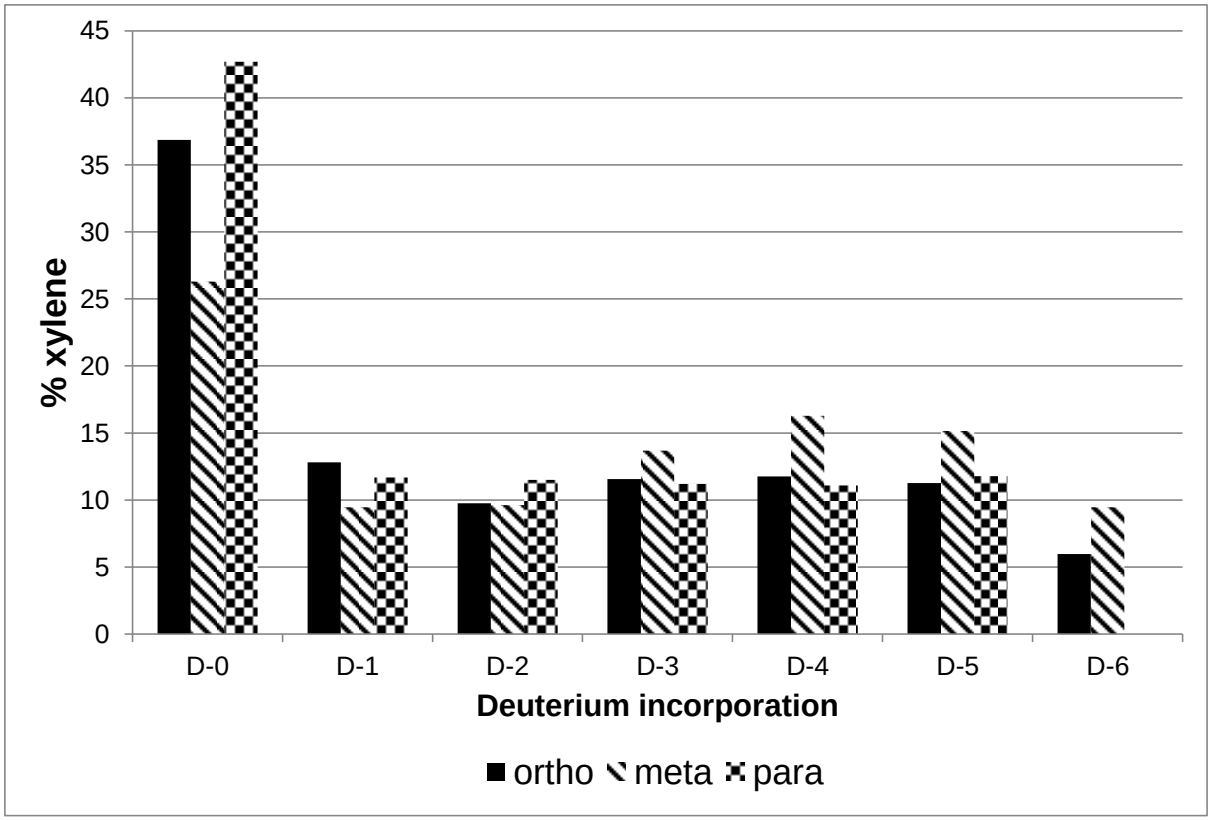


Figure 9. Ratio of isotopically exchanged methyl groups in *ortho*-, *meta*- and *para*-xylene after 15 min reaction. Conditions: 323 K, 3 barg deuterium, ~8 mmol.

Discussion

From the results presented in table 1 it can be seen that as the alkyl chain gets longer, the apparent activation energy increases and the order in organic becomes more negative, moving from zero order to negative first order. An apparent activation energy for toluene hydrogenation of 30 kJ.mol^{-1} has been reported over an Rh/MgO catalyst [5] in excellent agreement with our value. As expected as the alkyl chain length is increased the rate of hydrogenation decreases. It has been proposed that this decrease in rate is due the inductive effect of the alkyl chain increasing the electron density of the ring and hence resulting in a stronger π-bond to the surface [8,9,16,17], therefore suggesting that it is the strength of the

aromatic adsorption that is inhibiting the reaction. Our results confirm this hypothesis: the reaction order changes from zero-order with toluene to negative half-order with ethylbenzene to negative first-order with propylbenzene (table 1) indicating a stronger adsorption as the alkyl chain increases in length. (The stronger adsorption will also be confirmed from the competitive hydrogenation reactions to be discussed later.) The apparent activation energy for ethylbenzene hydrogenation was determined to be 46 $kJ.mol^{-1}$, while for the hydrogenation of propylbenzene a value of 39 $kJ.mol^{-1}$ was calculated.

The rate of hydrogenation of the xylenes gives an order *para* ≈ *ortho* > *meta* (table 1, figures 1-3), which is different from the order reported in the literature over platinum and nickel catalysts (*para* > *meta* > *ortho*) [9,11]. It is also noticeable that the rate of hydrogenation for the xylenes is faster than that of toluene (*meta*-xylene, the least active xylene, and toluene have similar rates, table 1). This is not what is generally reported in the literature, where toluene is usually more reactive than the xylenes, although *para*-xylene has been reported [11] to show a similar activity to toluene. The apparent activation energy calculated for *ortho*- and *meta*-xylene reveals a similar value (~ 26 $kJ.mol^{-1}$) a value that is much lower than that found by Keane and Patterson over nickel (~ 54 $kJ.mol^{-1}$) [9] and by Rahaman and Vannice over palladium (~ 51 $kJ.mol^{-1}$) [6]. *Para*-xylene in contrast gave a value of 42 $kJ.mol^{-1}$, which is similar to that found in the literature over Rh/MgO [5] of 36 $kJ.mol^{-1}$. In the work of Keane and Patterson [8, 9] a compensation effect was observed and our data would also show a similar trend. However more recent work on understanding this behaviour [18 – 20] has shown that behaviour does not represent a true correlation. A full reasoning can be found in the references [18 – 20]. Previous studies [5, 6] have looked for a relationship between ionisation potential and activation energy but we do not see any trend.

The cis:trans ratio of the dialkylcyclohexanes is shown in Figure 4 as a function of temperature. For the 1,4-dimethylcyclohexanes, the trans-isomer is the most stable and as the temperature is raised so the ease of formation of the trans-isomer increases resulting in a steady decrease in cis:trans ratio. For the 1,3-dimethylcyclohexanes it is the cis-isomer that is the most stable and the ratio is almost twice that found for the 1,4-dimethylcyclohexanes (figure 3 and 2). It is also clear that two intermediate dimethylcyclohexenes are formed; 3,5-dimethylcyclohex-1-ene, with this cyclohexene isomer the methyl groups are the furthest away from the surface minimising steric hindrance, and the more stable 1,3-dimethylcyclohex-1-ene where both methyl groups will be close to the surface. Nevertheless as the temperature is increased the ratio decreases at the same rate as the 1,4-isomers (figure 4). The behaviour of the 1,2-dimethylcyclohexanes with temperature is different. The trans-isomer is more stable but at low temperatures there is a significant cis excess (figure 1). This high cis:trans ratio, which has been observed with other rhodium catalysts [21], appears to be due to the hydrogenation of the 1,2-dimethylcyclohex-1-ene intermediate with all four positions surrounding the olefinic bond occupied by an alkyl species. As the temperature is raised the cis:trans ratio drops more rapidly than with the other systems until 323 K after which temperature the decrease in cis:trans ratio matches that of the 1,4- and 1,3-cyclohexanes (figure 4). Note that there is no evidence for isomerisation between species under reaction conditions. Therefore to yield the thermodynamically more stable trans-isomer the cyclohexene intermediate must desorb and re-adsorb with the sterically unfavourable cis configuration to the surface. The closer the methyl substituent is located to the double bond the higher the steric hindrance for the adsorbed surface species yielding the thermodynamically more stable trans product.

The competitive reactions between the alkylbenzenes were highly revealing. The competitive reaction between toluene and ethylbenzene reveals an increase in hydrogenation rate for both species (table 2). A previous study by Toppinen et al.[15] gave different results in that no increase in rate was observed but the general behaviour was similar. This enhanced rate behaviour is unusual but has been observed before in the competitive reaction of pentynes [22] and pentenes [23]. In both cases it was suggested that each species had a unique adsorption site that the other reactant could not influence and that the hydrogen flux could potentially be increased by enhanced hydrogen transfer from a hydrocarbonaceous deposit. Competitive hydrogenation of benzene and toluene has also been reported [10] and it was suggested that the sites for adsorption and hydrogenation of benzene and toluene were distinct from each other. It is noticeable that that the toluene/ethylbenzene reaction is the only pairing that results in an enhanced rate, all others reduce the rate of toluene and/or ethylbenzene hydrogenation (table 2). The reduction in rate caused by propylbenzene agrees with the kinetic analysis (table 1), which suggested that propylbenzene is much more strongly adsorbed than either toluene or ethylbenzene. In every case where propylbenzene is present the rates of hydrogenation for toluene and ethylbenzene are reduced by at least 58 %, in contrast, the rates of propylbenzene hydrogenation increase (table 2). In these reactions a reduction in the strength of propylbenzene adsorption would allow an enhancement in rate as in the absence of a second reactant, propylbenzene is an inhibitor.

The competitive reactions between the xylenes show completely different behaviour (table 3). In each competitive reaction the rate of hydrogenation was always decreased for all reactants. If the strength of bonding for the xylenes was similar then this behaviour would be expected, given that the reaction order for the xylenes is typically negative first order (table 1), as we would have increased the xylene concentration by a factor of two or three. The variations in

the activity from the competitive reactions suggest that the strength of bonding is ortho > para > meta. This agrees with the order of reactivity found by Toppinen et al. [15] in their study of xylene competitive hydrogenation. The higher cis:trans ratio for the 1,2-dimethylcyclohexanes is expected as the higher aromatic concentration would tend to inhibit re-adsorption to allow for isomerisation.

When hydrogenation reactions are performed using deuterium rather than hydrogen two processes may occur, exchange and hydrogenation. The exchange process of toluene and the xylenes have been well studied [24,25]. In general the alkyl groups exchange before the ring hydrogens. However, although well studied, the exchange process has not been examined over rhodium. With toluene the ratio of the aliphatic:aromatic peaks in the reaction setting is not the same as in the reference sample. In the reference sample the ratio of peaks is 1.8 whereas in the reaction sample the ratio is 2.5 (figure 7 and Supplementary Information). Therefore the rate of exchange of the protons in the methyl group is faster than that of the aromatic protons, which contrasts with the exchange over palladium [25], where only the methyl groups were exchanged but is more similar to nickel where both sets of hydrogen exchanged but the rate of methyl group exchange was over an order of magnitude faster [24]. The reverse process, hydrogen exchange with d_8-toluene appears to be slower (Figure 8) possibly displaying a kinetic isotope effect, with d_8-toluene still present 10 min into the reaction. The exchange of the xylenes shows only exchange into the two methyl groups similar to that found with palladium [25]. Para-xylene has the highest quantity of d-0 species (figure 9) and this is similar to the distribution found over nickel for the exchange process [24].

The hydrogenation of toluene and the xylenes using deuterium results in a kinetic isotope effect. All the reactants except *ortho*-xylene exhibit an inverse kinetic isotope effect (KIE) (table 5). This is likely a secondary inverse KIE which can be observed when there is a change in hybridisation of the carbon (C-H) from sp^2 to sp^3 as would be the case in hydrogenation of the aromatic ring. The difference with *ortho*-xylene and identifying 1,2-dimethylcyclohexene as the main intermediate raises the question of whether the rate determining step is different from that of toluene and *meta*- and *para*-xylene.

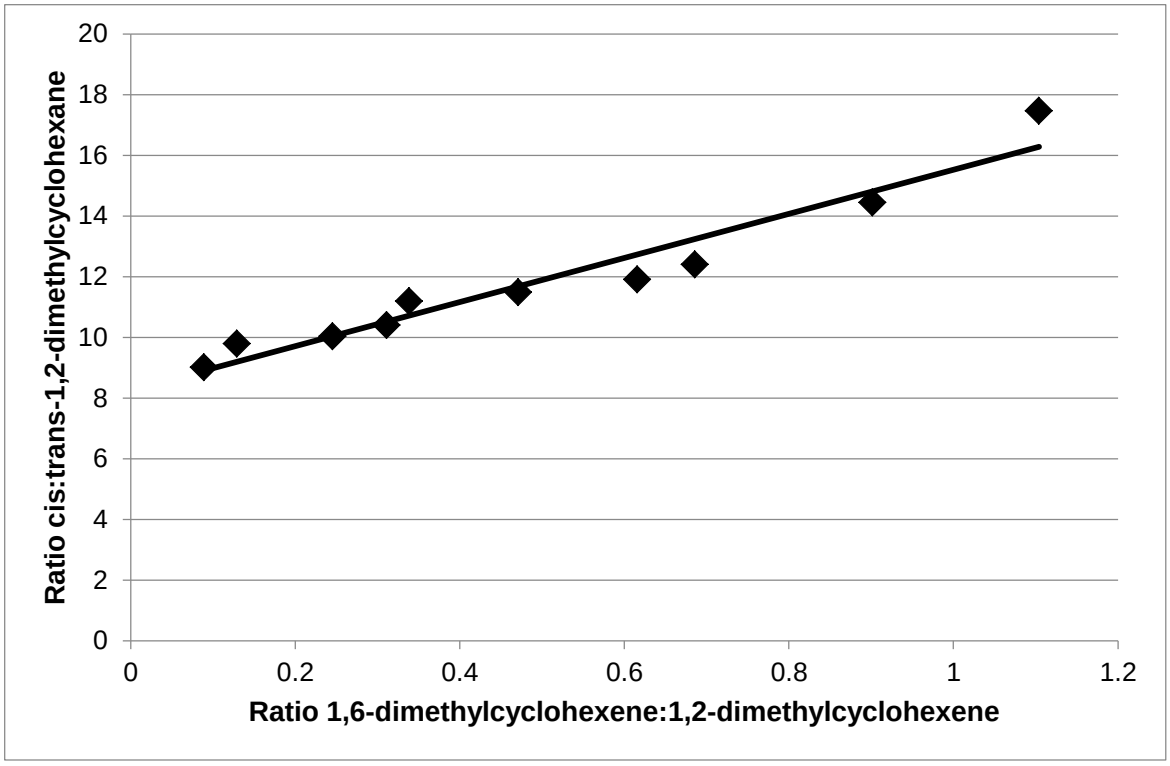


Figure 10. Relationship between dimethylcyclohexene intermediates and cis- and trans-1,2-dimethlcyclohexanes, showing line of best fit.

Two dimethylcyclohexenes were detected and when the cis:trans ratio of the 1,2-dimethylcyclohexanes is compared with the ratio of the 1,6:1,2-dimethyl cyclohexenes (Figure 10) it can be seen that there is a relationship, suggesting that one intermediate produces the cis-product while the other produces the trans-product. Indeed this can be

confirmed with a simple model, addition of hydrogen from below to 1,2-dimethylcyclohexene generates cis-1,2-dimethylcyclohexane, whereas a similar addition to 1,6-dimethylcyclohexene results in trans-1,2-dimethylcyclohexane.

Conclusions

In this study the hydrogenation of toluene, ethylbenzene, propylbenzene and the xylenes has been investigated over a rhodium catalyst for the first time. Kinetic analysis revealed that the order of reaction in hydrogen was typically first order while the reaction order in the aromatic varied between zero order and negative first order. Activation energies were determined but no trends were evident. The competitive hydrogenation between toluene, ethylbenzene and propylbenzene revealed that the propylbenzene was the most strongly adsorbed aromatic in agreement with the strongly negative reaction order. The xylenes gave an order of reactivity of *para* > *ortho* > *meta* following the increasing negative reaction order. Reactions with deuterium revealed an inverse kinetic isotope effect (KIE) for all reactions, except that of *ortho*-xylene, suggesting that hydrogen bond breaking or making is not rate limiting. The cause of the inverse KIE is most likely related to the change in hybridization of the carbon (C-H) from sp^2 to sp^3. Rapid exchange of the methyl group hydrogens was observed with all the xylenes, whereas total exchange was noted with toluene. The generation of trans-1,2-dimethylcyclohexane was explained by the formation of two intermediates, 1,2-dimethylcyclohexene and 1,6-dimethylcyclohexene, which give the cis-1,2-dimethylcyclohexane and trans-1,2-dimethylcyclohexane respectively.

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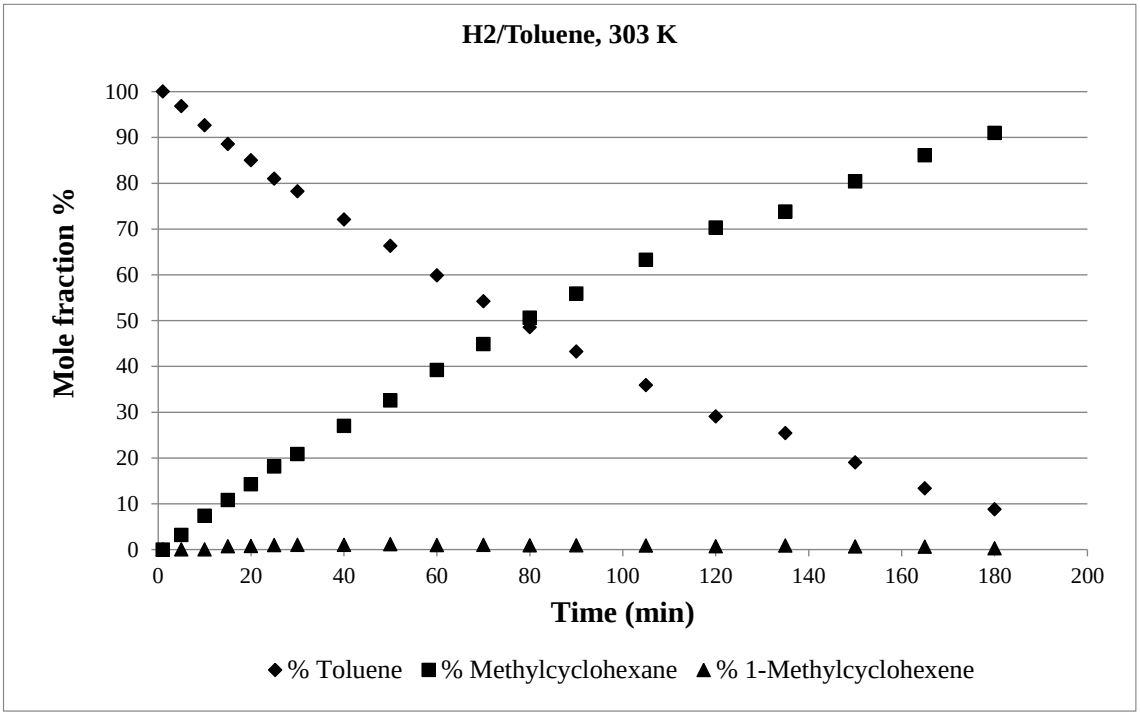
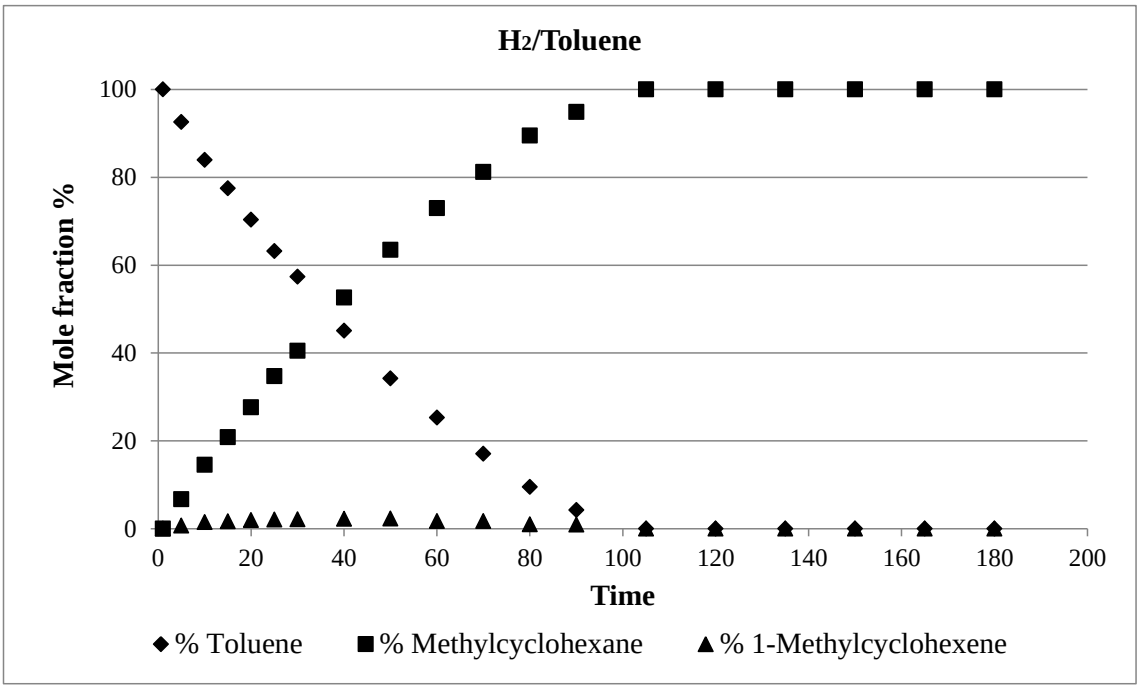
Supplementary Data for Hydrogenation of Alkylaromatics over Rh/silica.

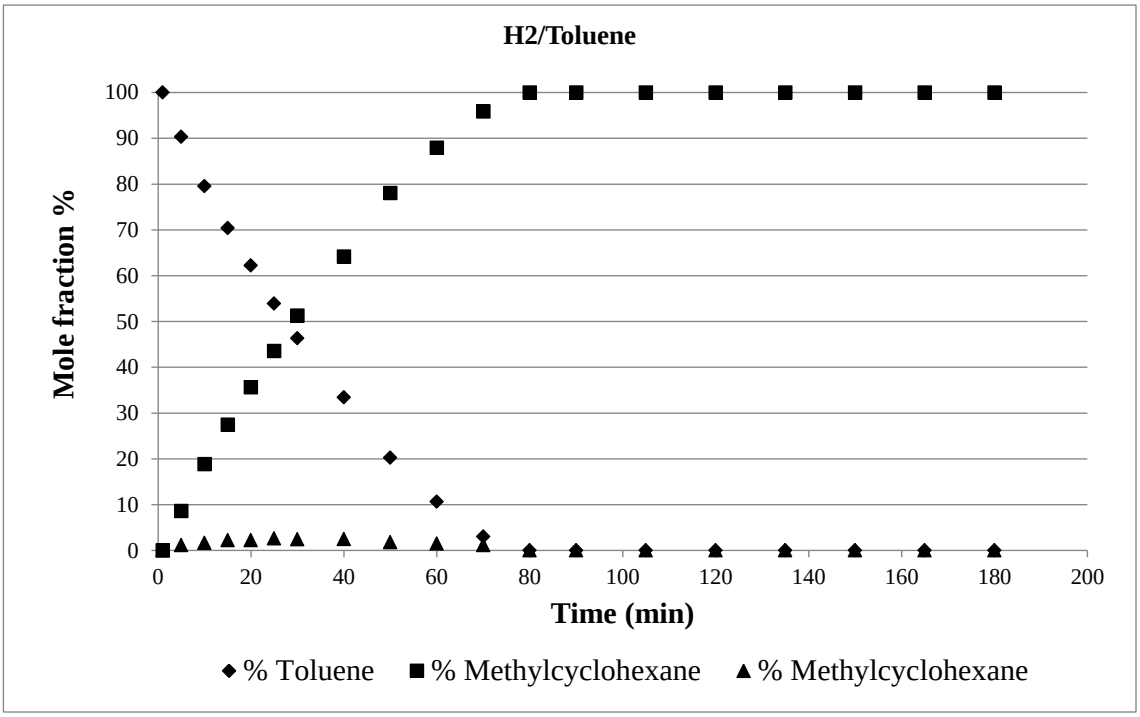
Toluene hydrogenation at 303 K, 3 barg and ~8 mmol.



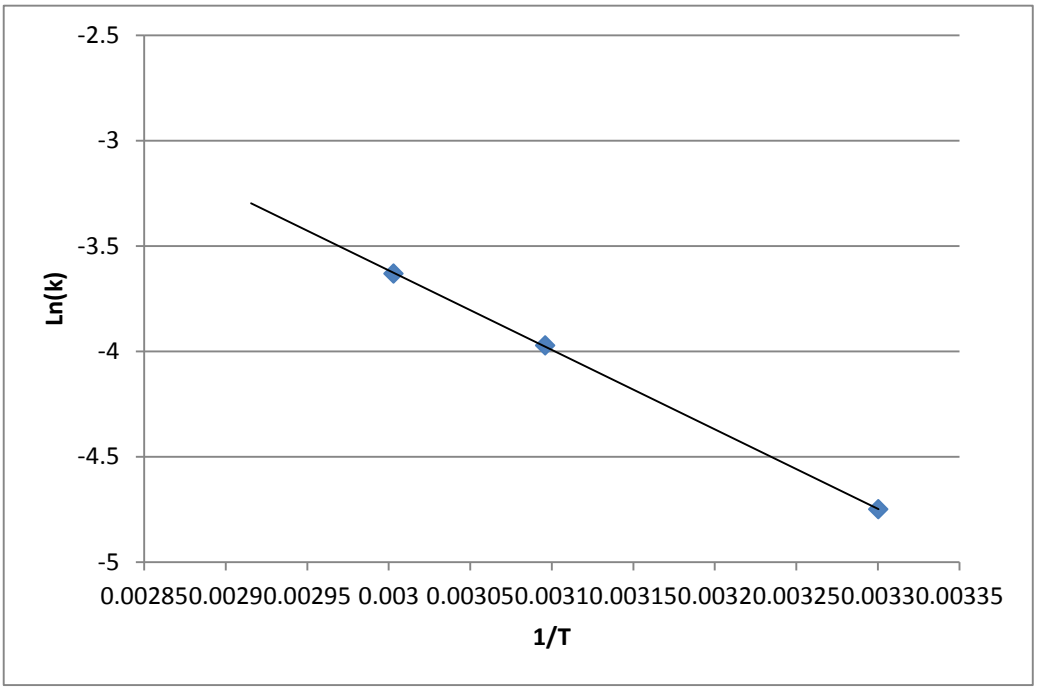
Toluene hydrogenation at 323 K, 3 barg and ~8 mmol.



Toluene hydrogenation at 333 K, 3 barg and ~8 mmol



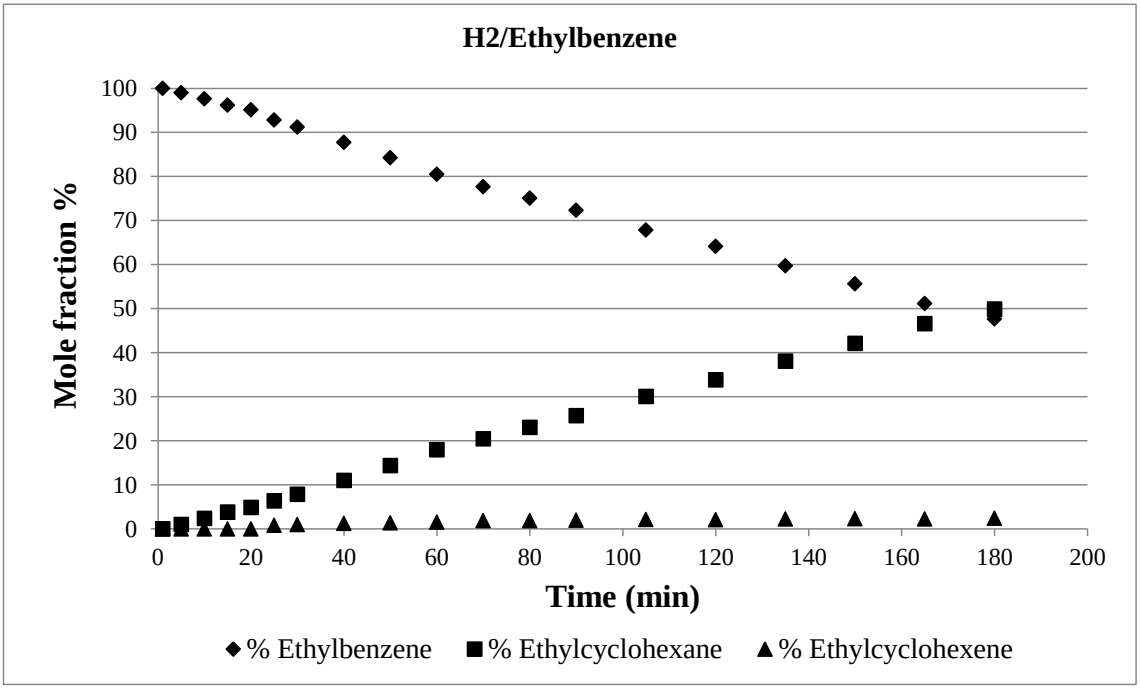
Toluene activation energy plot



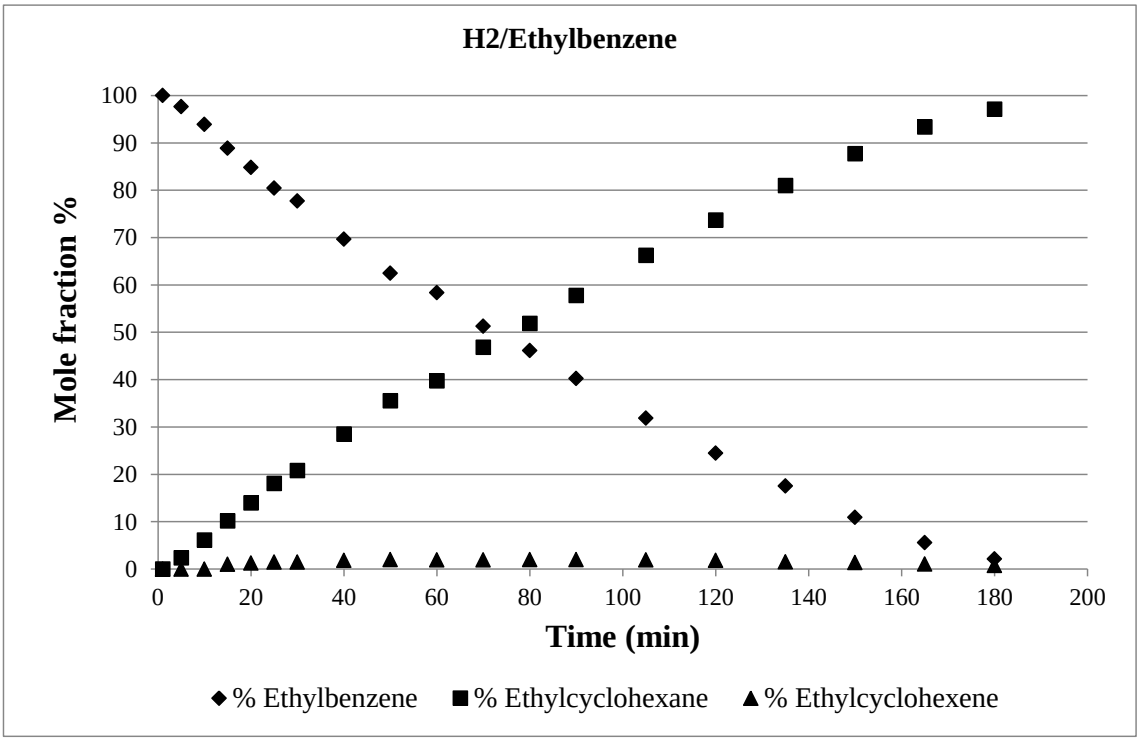
Determination of activation energy for toluene

toluene				Regression Output:		
			Constant			7.69961133497827
1/T	ln(k)		Std Err of Y Est			0.00749111280722702
0.0033	-4.7502		R Squared			0.999914563873391
0.003096	-3.97284		No. of Observations			3
0.003003	-3.63212		Degrees of Freedom			1
			X Coefficient(s)		-3772.10277741635	
			Std Err of Coef.		34.8676634687996	
Ea =	31.3612624914396					
	0.2898897540796					

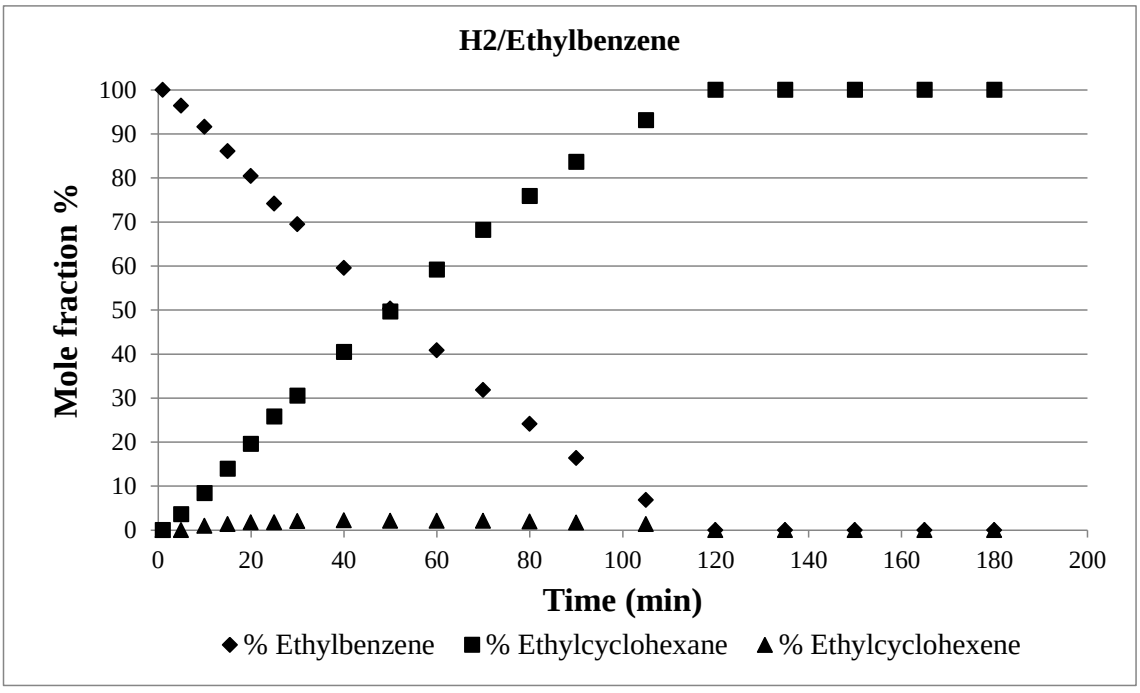
Ethylbenzene hydrogenation at 303 K, 3 barg and ~8 mmol.



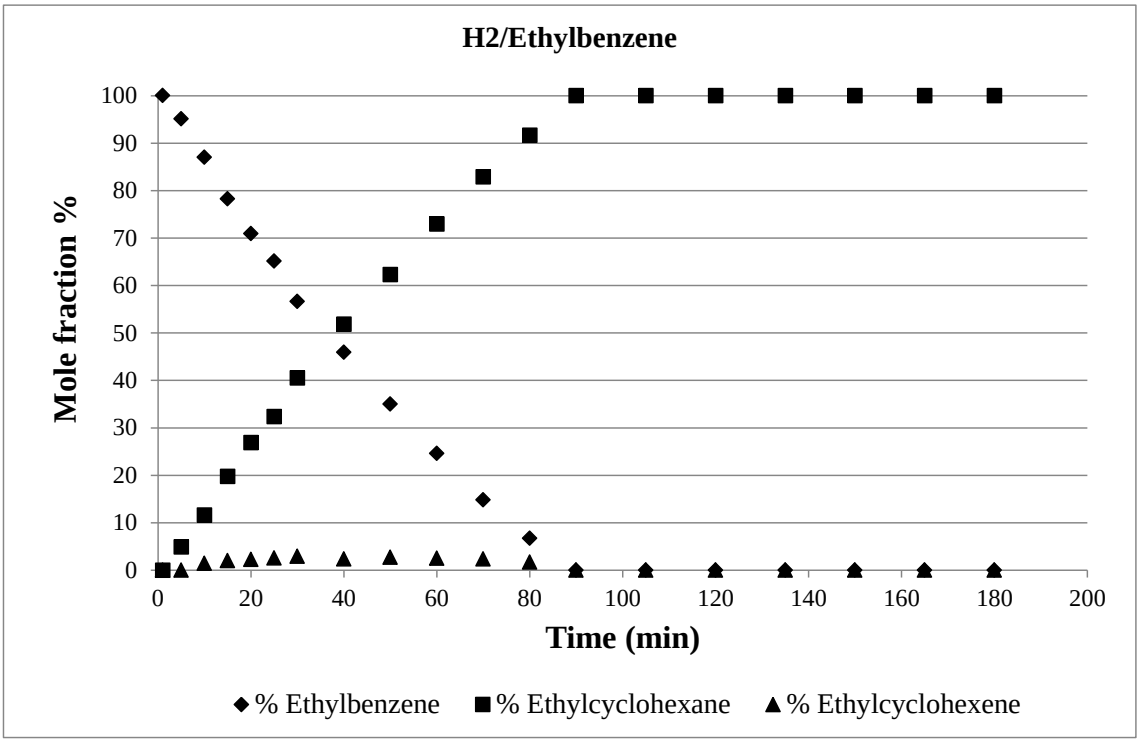
Ethylbenzene hydrogenation at 313 K, 3 barg and ~8 mmol.



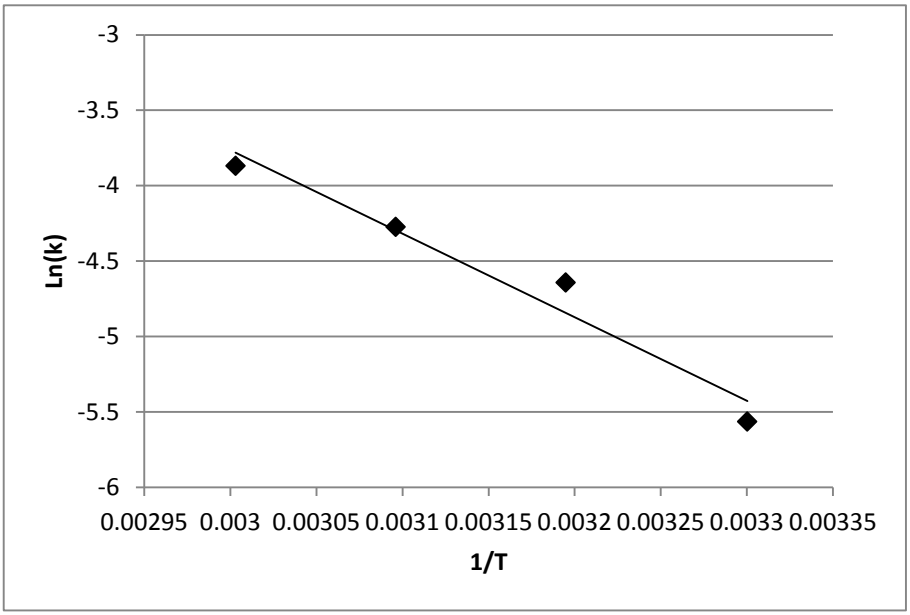
Ethylbenzene hydrogenation at 323 K, 3 barg and ~8 mmol.



Ethylbenzene hydrogenation at 333 K, 3 barg and ~8 mmol.



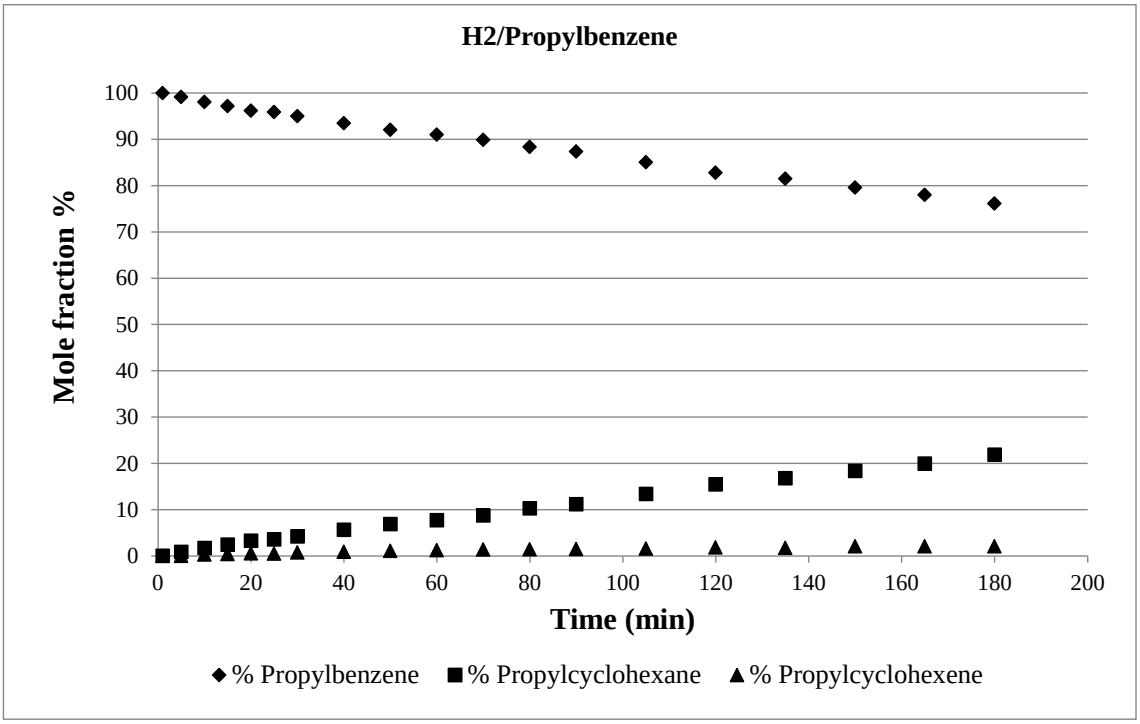
Ethylbenzene activation energy plot



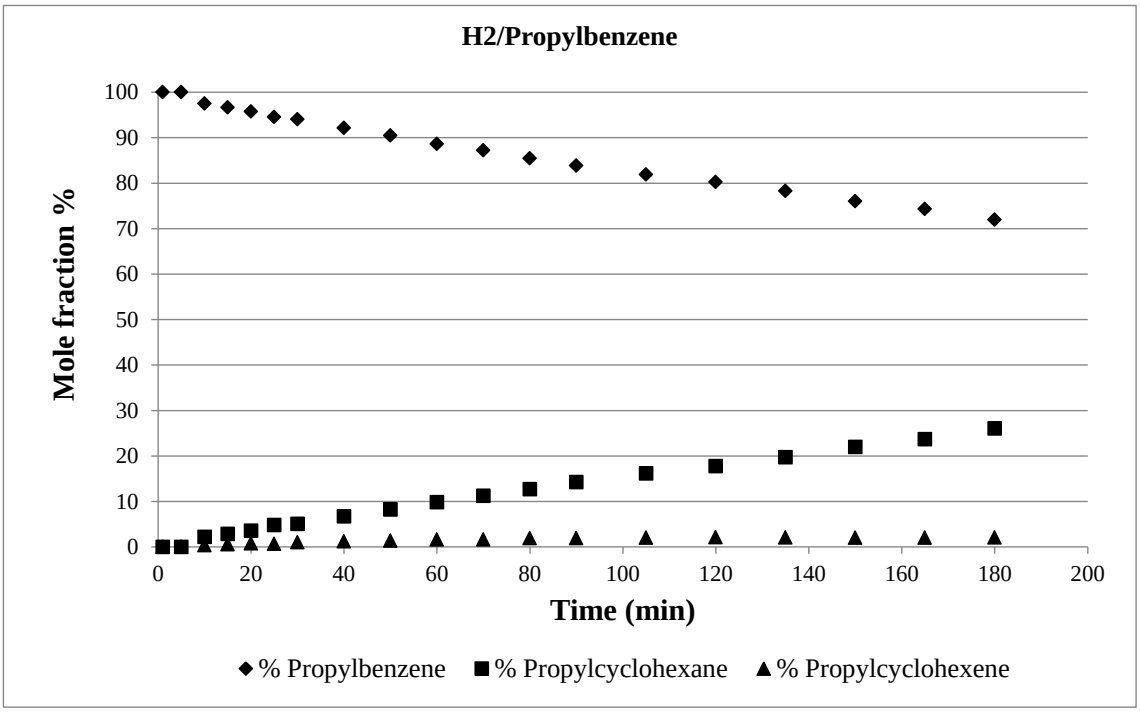
Determination of activation energy for ethylbenzene

ethylbenzene				Regression Output:		
			Constant			12.861389
			Std Err of Y Est			0.1841621
1/T	ln(k)		R Squared			0.956907
0.0033	-5.56489		No. of Observations			4
0.003195	-4.64318		Degrees of Freedom			2
0.003096	-4.27443					
0.003003	-3.86801		X Coefficient(s)		-5542.009	
			Std Err of Coef.		831.61181	
Ea =	46.076265					
+/-	6.9140206					

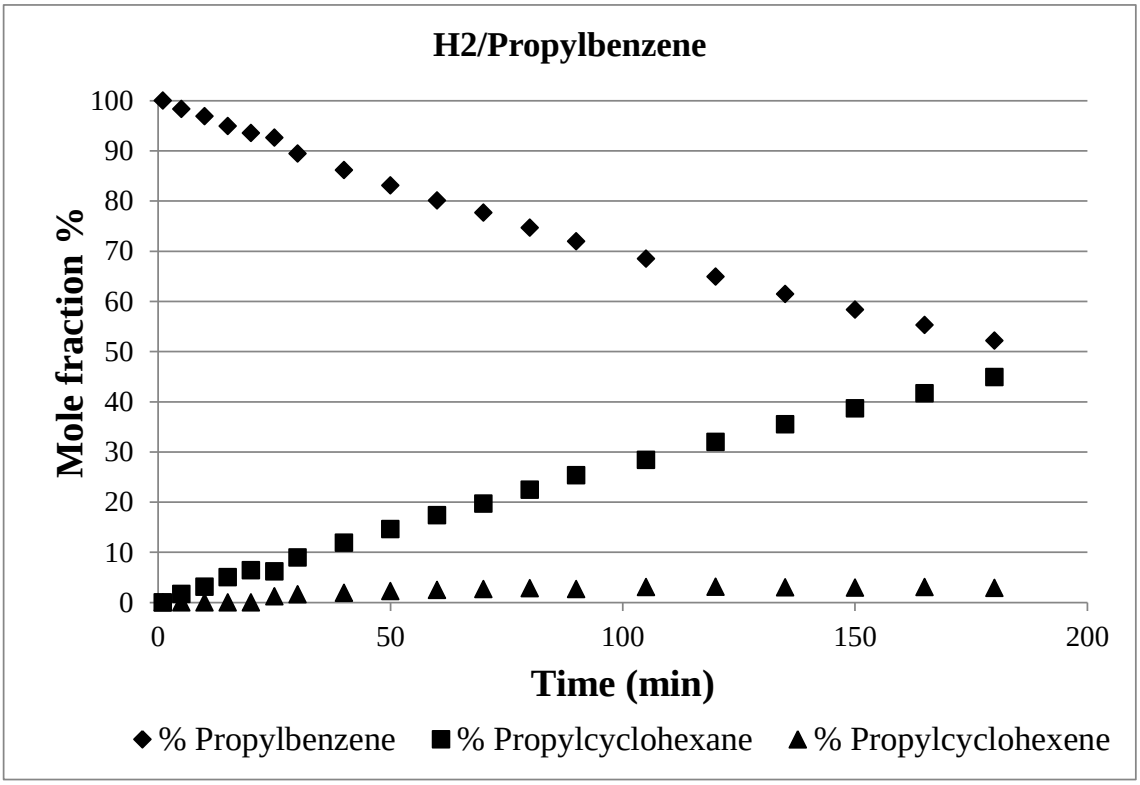
Propylbenzene hydrogenation at 308 K, 3 barg and ~8 mmol.



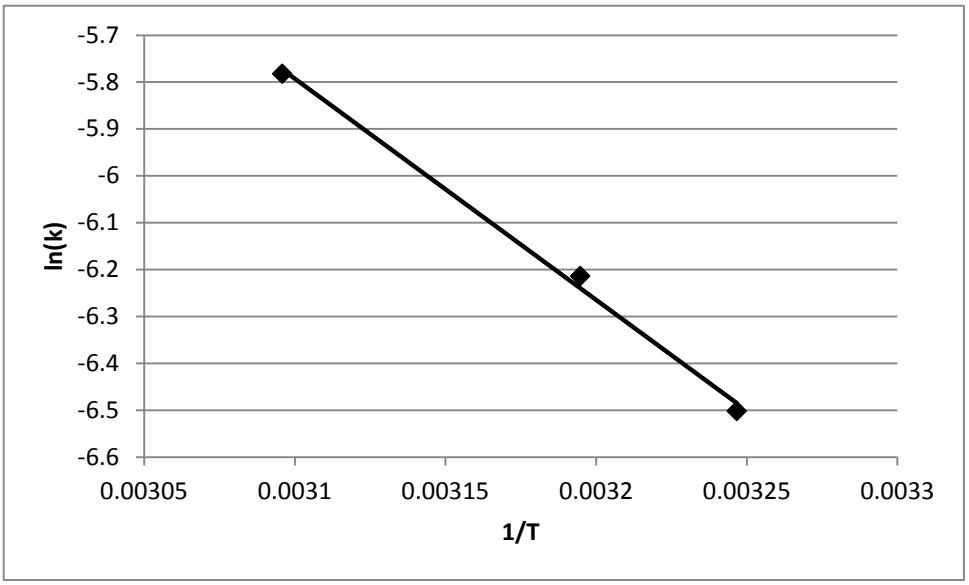
Propylbenzene hydrogenation at 313 K, 3 barg and ~8 mmol.



Propylbenzene hydrogenation at 323 K, 3 barg and ~8 mmol.



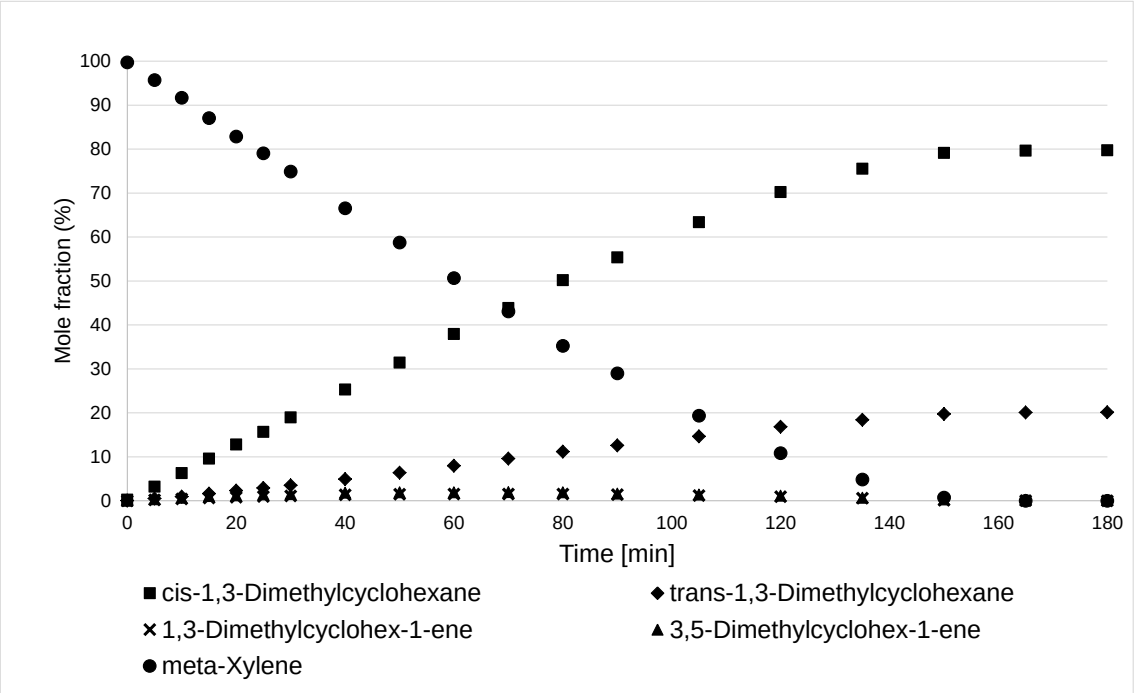
Propylbenzene activation energy plot



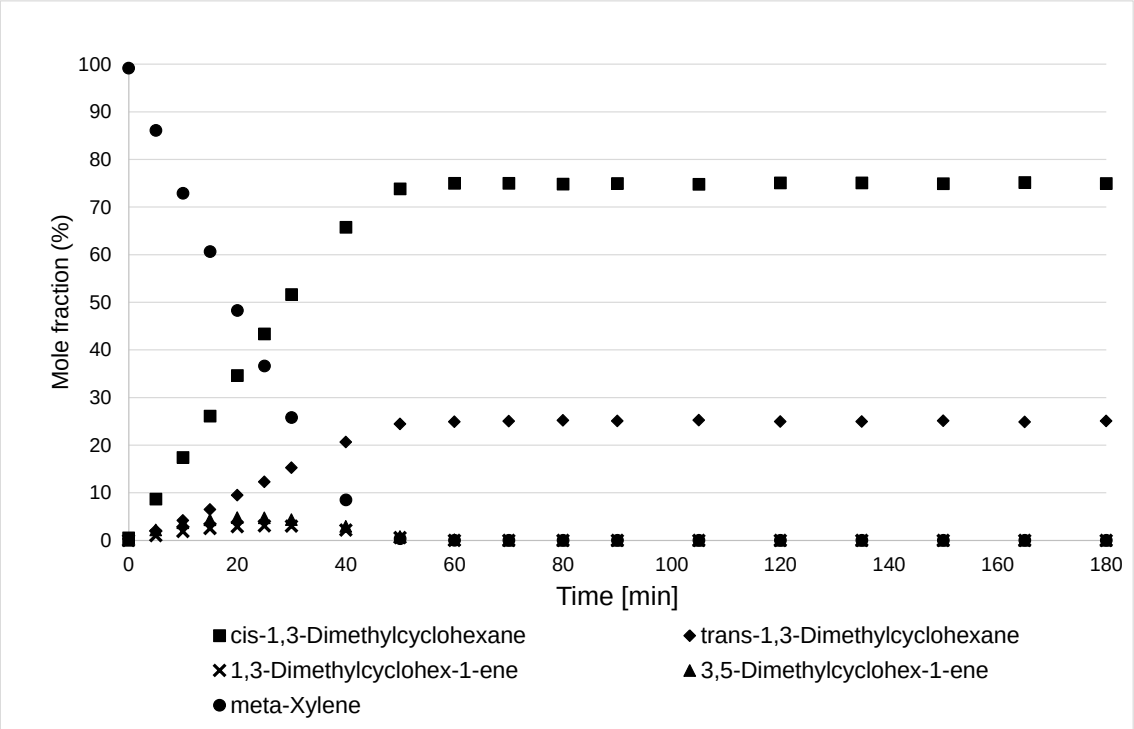
Determination of activation energy for propylbenzene

propylbenzene						
				Regression Output:		
			Constant			8.8128362
1/T			Std Err of Y Est			0.0320798
0.003247	-6.50229		R Squared			0.9960762
0.003195	-6.21461		No. of Observations			3
0.003096	-5.78283		Degrees of Freedom			1
			X Coefficient(s)		-4711.495	
			Std Err of Coef.		295.7114	
Ea =	39.171369					
+/-	2.4585446					

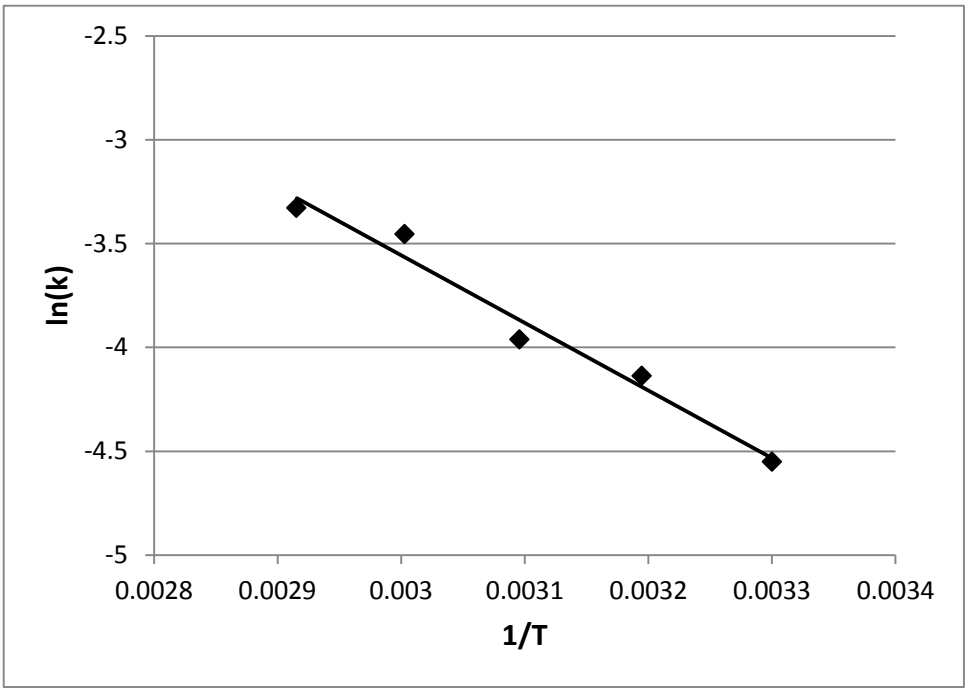
meta-xylene hydrogenation at 303 K, 3 barg hydrogen and ~8 mmol.



meta-xylene hydrogenation at 333 K, 3 barg hydrogen and ~8 mmol.



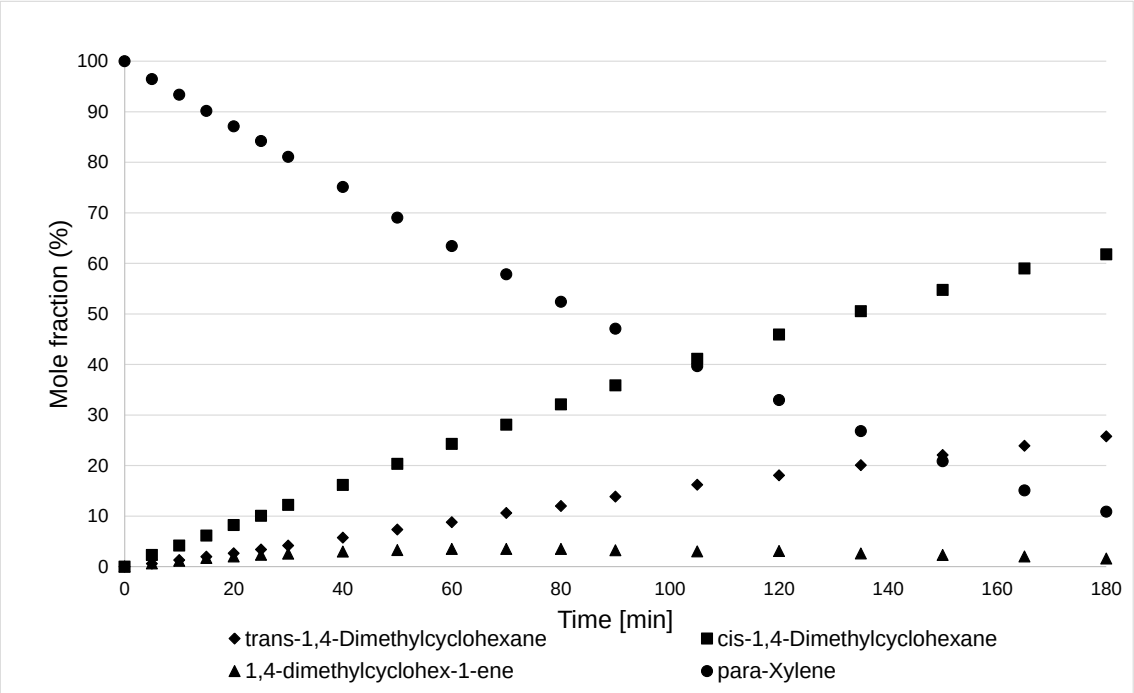
meta-xylene activation energy plot



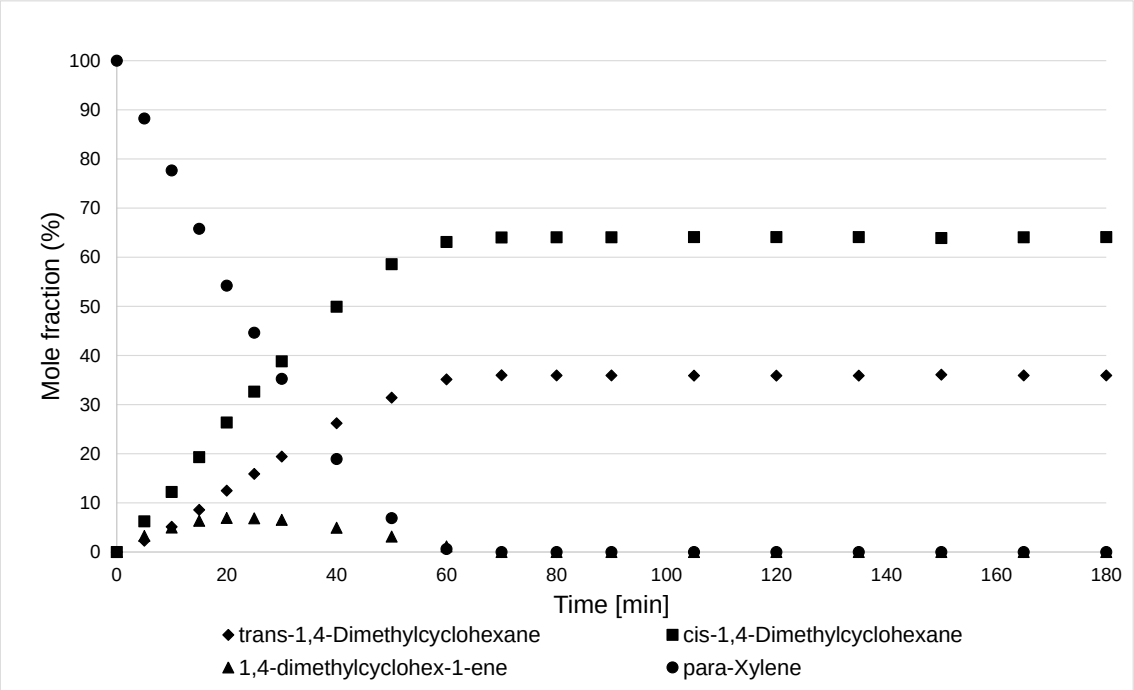
Determination of activation energy for meta-xylene

meta-xylene							
					Regression Output:		
				Constant			6.2085586
1/T	k	ln(k)		Std Err of Y Est			0.0941406
0.0033	1.06E-002	-4.55163		R Squared			0.9736315
0.003195	1.59E-002	-4.13892		No. of Observations			5
0.003096	1.90E-002	-3.96332		Degrees of Freedom			3
0.003003	3.16E-002	-3.45586					
0.002915	3.58E-002	-3.32897		X Coefficient(s)		-3254.981	
				Std Err of Coef.		309.26699	
Ea =	27.061908						
	2.5712457						

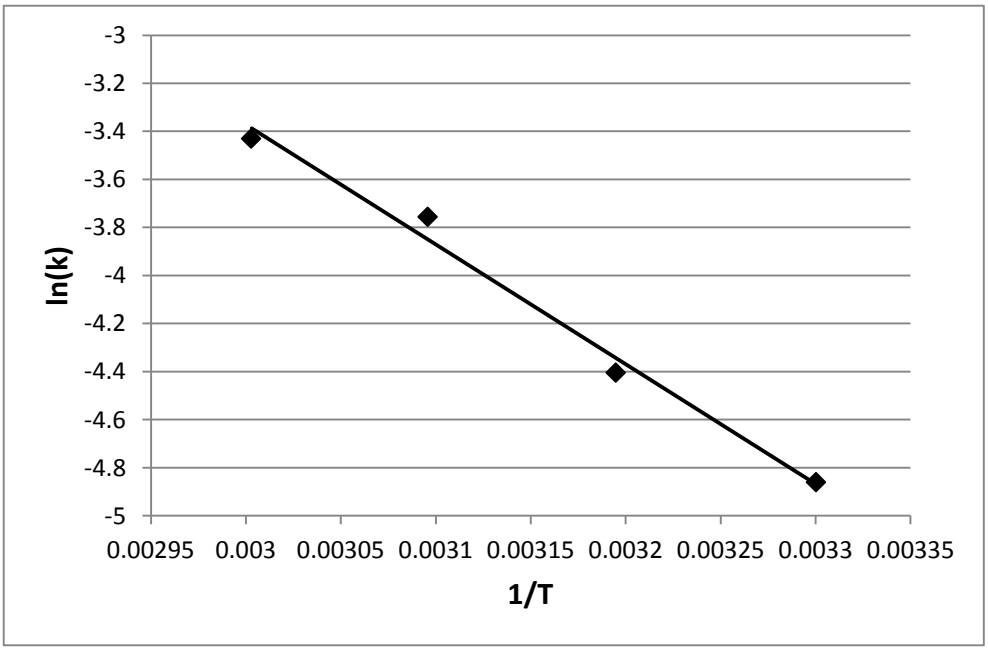
para-xylene hydrogenation at 303 K, 3 barg hydrogen and ~8 mmol.



Para-xylene hydrogenation at 333 K, 3 barg hydrogen and ~8 mmol.



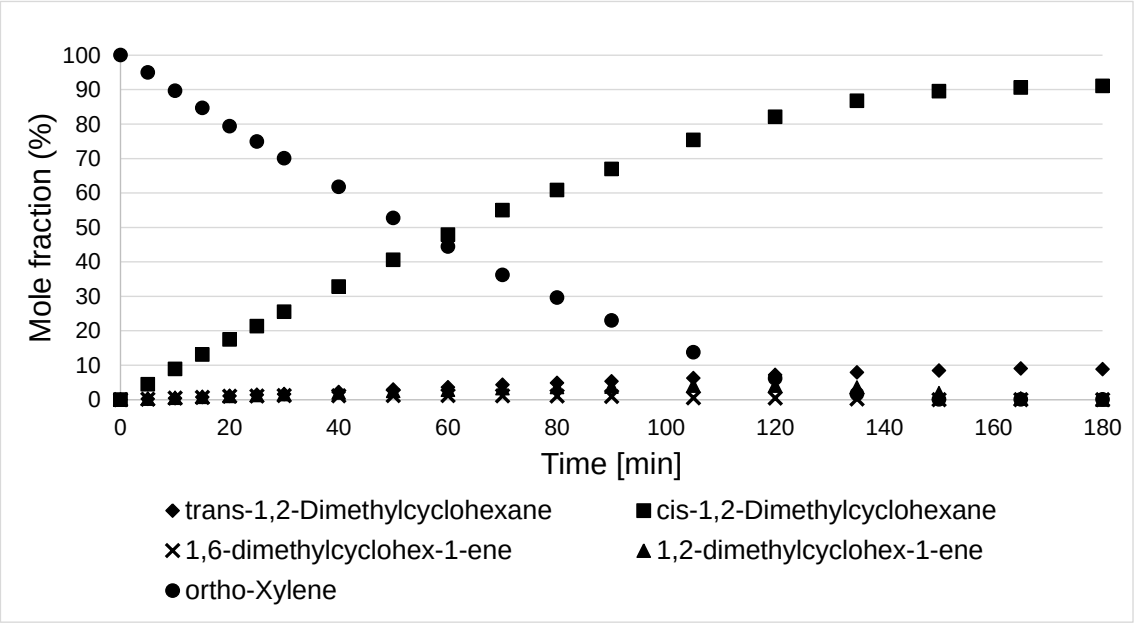
para-xylene activation energy plot



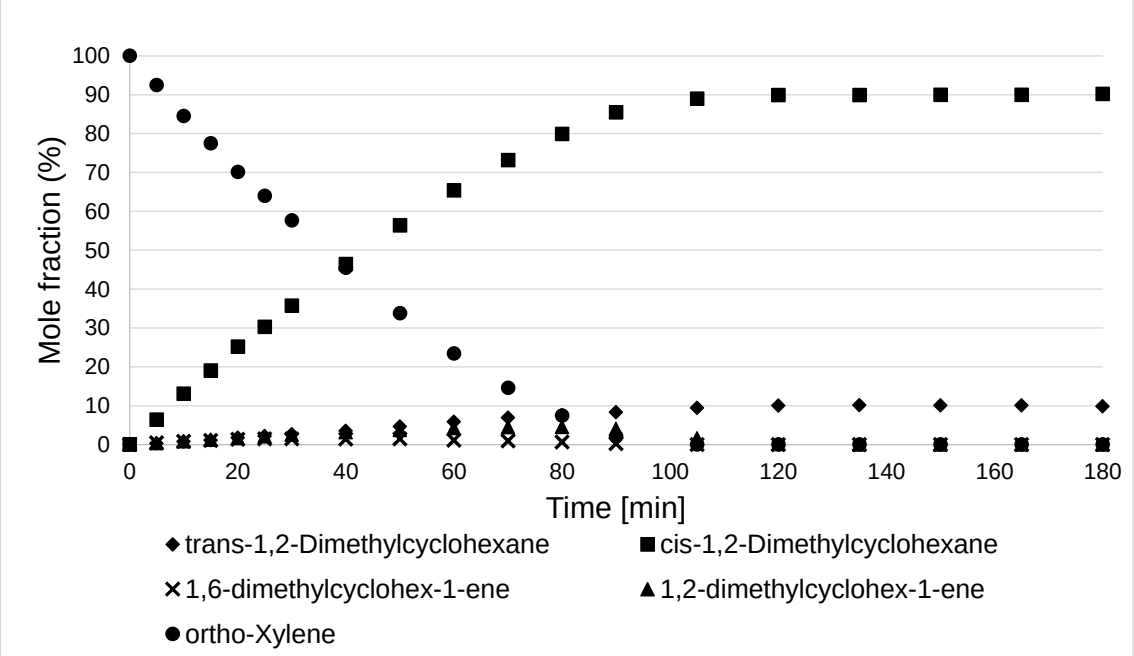
Determination of activation energy for para-xylene

para-xylene							
					Regression Output:		
				Constant			11.602749
1/T	k	ln(k)		Std Err of Y Est			0.085475
0.0033	7.75E-003	-4.86032		R Squared			0.9881824
0.003195	1.22E-002	-4.40468		No. of Observations			4
0.003096	2.34E-002	-3.75587		Degrees of Freedom			2
0.003003	3.24E-002	-3.43083					
				X Coefficient(s)		-4991.48	
				Std Err of Coef.		385.97547	
Ea =	41.499163						
	3.209						

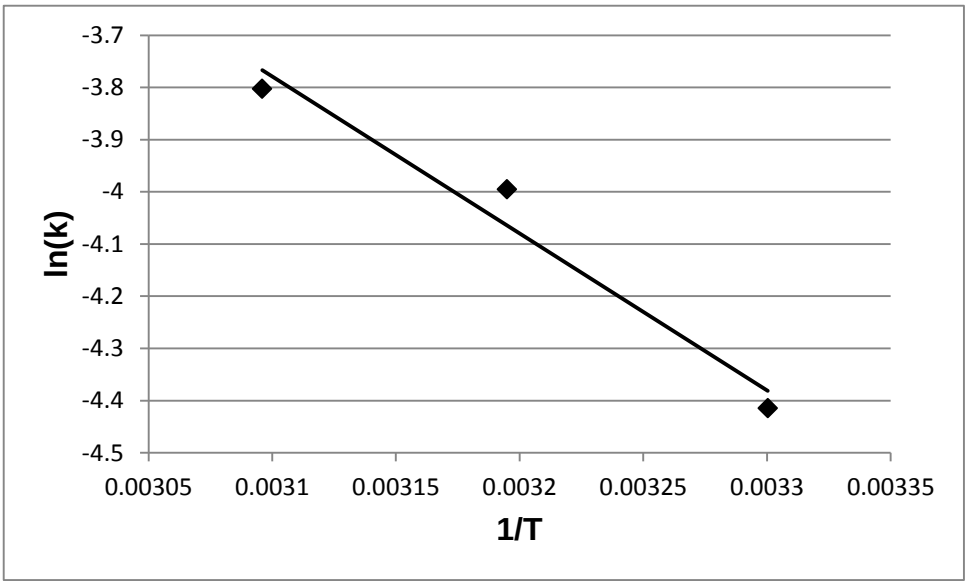
Ortho-xylene hydrogenation at 303 K, 3 barg hydrogen and ~8 mmol.



Ortho-xylene hydrogenation at 313 K, 3 barg hydrogen and ~8 mmol.



Ortho-xylene activation energy plot



Determination of activation energy for ortho-xylene

ortho-xylene							
					Regression Output:		
				Constant			5.5494673
1/T	k	ln(k)		Std Err of Y Est			0.0850973
0.0033	1.21E-002	-4.41455		R Squared			0.9629997
0.003195	1.84E-002	-3.9954		No. of Observations			3
0.003096	2.23E-002	-3.80272		Degrees of Freedom			1
0.003003	1.22E-002	-4.40632					
0.002915	1.21E-002	-4.41455		X Coefficient(s)		-3009.183	
				Std Err of Coef.		589.8451	
Ea =	25.018345						
	4.9039722						

The rate constants at 323 K reported in table 1 were calculated as shown below.

toluene				Regression Output:		
			Constant			-0.008571
time in min	1st order		Std Err of Y Est			0.0088641
0	0		R Squared			0.9978562
5	0.08		No. of Observations			6
10	0.17		Degrees of Freedom			4
15	0.26					
20	0.35		X Coefficient(s)		0.0182857	
25	0.46		Std Err of Coef.		0.0004238	
ethylbenzene				Regression Output:		
			Constant			-0.019643
time in min	1st order		Std Err of Y Est			0.0147115
0	0		R Squared			0.9899775
5	0.04		No. of Observations			7
10	0.09		Degrees of Freedom			5
15	0.15					
20	0.22		X Coefficient(s)		0.0123571	
25	0.3		Std Err of Coef.		0.000556	
30	0.36					
propylbenzene				Regression Output:		
			Constant			0.0009524
time in min	1st order		Std Err of Y Est			0.0032367
0	0		R Squared			0.9910524
5	0.02		No. of Observations			6
10	0.03		Degrees of Freedom			4
15	0.05					
20	0.07		X Coefficient(s)		0.0032571	
25	0.08		Std Err of Coef.		0.0001547	

ortho-xylene				Regression Output:		
			Constant			-0.011146
time in min	1st order		Std Err of Y Est			0.0092024
0	0		R Squared			0.9987857
5	0.1001048		No. of Observations			7
10	0.205678		Degrees of Freedom			5
15	0.3109514					
20	0.4340907		X Coefficient(s)		0.0223056	
25	0.5451259		Std Err of Coef.		0.0003478	
30	0.6681077					
para-xylene				Regression Output:		
			Constant			-0.016427
time in min	1st order		Std Err of Y Est			0.0143582
0	0		R Squared			0.9965631
5	0.0956445		No. of Observations			6
10	0.2052325		Degrees of Freedom			4
15	0.3190951					
20	0.4549456		X Coefficient(s)		0.0233782	
25	0.5798831		Std Err of Coef.		0.0006865	
meta-xylene				Regression Output:		
			Constant			-0.018606
time in min	1st order		Std Err of Y Est			0.0179573
0	0		R Squared			0.9913121
5	0.0712045		No. of Observations			6
10	0.1476227		Degrees of Freedom			4
15	0.2364839					
20	0.3544012		X Coefficient(s)		0.0183414	
25	0.4542581		Std Err of Coef.		0.0008585	

For the competitive reactions (table 2 and table 3) the rate constants were calculated as shown below.

toluene/propylbenzene				toluene	Regression Output:		
				Constant			-0.003929
time in mi	1st order	1st order		Std Err of Y Est			0.005278
0	0	0		R Squared			0.9961914
5	0.03	0.03		No. of Observations			7
10	0.06	0.07		Degrees of Freedom			5
15	0.11	0.1					
20	0.14	0.14		X Coefficient(s)		7.21E-003	
25	0.18	0.18		Std Err of Coef.		1.99E-004	
30	0.21	0.21					
40		0.29					
50		0.36		propylb	Regression Output:		
				Constant			-0.00438
				Std Err of Y Est			0.0034342
				R Squared			0.9992758
				No. of Observations			9
				Degrees of Freedom			7
				X Coefficient(s)		7.28E-003	
				Std Err of Coef.		7.41E-005	
toluene/ethylbenzene				toluene	Regression Output:		
				Constant			-0.021071
time in mi	1st order	1st order		Std Err of Y Est			0.0149045
0	0	0		R Squared			0.9964867
5	0.08	0.06		No. of Observations			7
10	0.18	0.14		Degrees of Freedom			5
15	0.28	0.22					
20	0.4	0.32		X Coefficient(s)		2.12E-002	
25	0.51	0.4		Std Err of Coef.		5.63E-004	
30	0.63	0.5					
40							
50				ethylb	Regression Output:		
				Constant			-0.018571
				Std Err of Y Est			0.0130931
				R Squared			0.9957094
				No. of Observations			7
				Degrees of Freedom			5
				X Coefficient(s)		1.69E-002	
				Std Err of Coef.		4.95E-004	

ethylbenzene/propylbenzene				ethylb	Regression Output:		
				Constant			-0.005698
time in	mi 1st order	1st order		Std Err of Y Est			0.0058828
0	0	0		R Squared			0.9945138
5	0.02	0.03		No. of Observations			9
10	0.04	0.05		Degrees of Freedom			7
15	0.06	0.08					
20	0.08	0.11		X Coefficient(s)		4.52E-003	
25	0.1	0.13		Std Err of Coef.		1.27E-004	
30	0.13	0.16					
40	0.17	0.22					
50	0.23	0.3		propylb	Regression Output:		
				Constant			-0.000802
				Std Err of Y Est			0.0034924
				R Squared			0.9980086
				No. of Observations			8
				Degrees of Freedom			6
				X Coefficient(s)		5.42E-003	
				Std Err of Coef.		9.89E-005	

toluene/ethylbenzene/propylbenzene					toluene	Regression Output:		
					Constant			-0.00375
time in	mi 1st order	1st order	1st order		Std Err of Y Est			0.0037268
0	0	0	0		R Squared			0.9986892
5	0.02	0.01	0.02		No. of Observations			11
10	0.04	0.03	0.04		Degrees of Freedom			9
15	0.06	0.04	0.05					
20	0.08	0.05	0.07		X Coefficient(s)		4.25E-003	
25	0.1	0.07	0.09		Std Err of Coef.		5.13E-005	
30	0.12	0.08	0.13					
40	0.16	0.11	0.16					
50	0.21	0.15	0.21		ethylb	Regression Output:		
60	0.25		0.25		Constant			-0.003488
70	0.3		0.29		Std Err of Y Est			0.0044647
					R Squared			0.9924981
					No. of Observations			9
					Degrees of Freedom			7
					X Coefficient(s)		2.93E-003	
					Std Err of Coef.		9.63E-005	
					propylb	Regression Output:		
					Constant			-0.005841
					Std Err of Y Est			0.0067965
					R Squared			0.9956096
					No. of Observations			11
					Degrees of Freedom			9
					X Coefficient(s)		4.23E-003	
					Std Err of Coef.		9.36E-005	

ortho/para					ortho	Regression Output:		
					Constant			-0.008101
time in	mino	p			Std Err of Y Est			0.0054085
0	0	0			R Squared			0.9984659
5	0.0321167	0.0102527			No. of Observations			9
10	0.0689389	0.0254592			Degrees of Freedom			7
15	0.1091747	0.043795						
20	0.1447409	0.0591649			X Coefficient(s)		7.87E-003	
25	0.1850303	0.0770565			Std Err of Coef.		1.17E-004	
30	0.2231007	0.09029						
40	0.305173	0.1241907						
50	0.3940529	0.1648443			para	Regression Output:		
		0.1993185			Constant			-0.005415
					Std Err of Y Est			0.003399
					R Squared			0.9965609
					No. of Observations			9
					Degrees of Freedom			7
					X Coefficient(s)		3.30E-003	
					Std Err of Coef.		7.33E-005	
ortho/meta					ortho	Regression Output:		
					Constant			-0.003615
time in	mino	m			Std Err of Y Est			0.0022139
0	0	0			R Squared			0.9993712
5	0.018869	0.0062821			No. of Observations			9
10	0.0467927	0.0138318			Degrees of Freedom			7
15	0.0699843	0.0231978						
20	0.0982494	0.0321018			X Coefficient(s)		5.04E-003	
25	0.1204746	0.0411653			Std Err of Coef.		4.77E-005	
30	0.1489525	0.0537374						
40	0.1965963	0.0713196						
50	0.2495619	0.0905298			meta	Regression Output:		
					Constant			-0.003235
					Std Err of Y Est			0.0018724
					R Squared			0.9966857
					No. of Observations			9
					Degrees of Freedom			7
					X Coefficient(s)		1.85E-003	
					Std Err of Coef.		4.04E-005	

ortho/meta/para								
	o	m	p		ortho	Regression Output:		
time in min	first order	first order	first order		Constant			-0.003842
0	0	0	0		Std Err of Y Est			0.0025356
5	0.0231292	0.006957	0.0123959		R Squared			0.999289
10	0.0453523	0.0137298	0.0199232		No. of Observations			9
15	0.0777274	0.0227405	0.0350475		Degrees of Freedom			7
20	0.1048393	0.0303604	0.0461023					
25	0.1314002	0.0386263	0.0607858		X Coefficient(s)		5.42E-003	
30	0.1600812	0.0478268	0.0740465		Std Err of Coef.		5.47E-005	
40	0.2119258	0.0624471	0.0980173					
50	0.268655	0.0792995	0.1257881					
60	0.3263045	0.0971248	0.1507306		meta	Regression Output:		
	0.386583	0.1146196	0.1807047		Constant			-0.001119
	0.4476519		0.2118624		Std Err of Y Est			0.0007743
					R Squared			0.9992385
					No. of Observations			9
					Degrees of Freedom			7
					X Coefficient(s)		1.60E-003	
					Std Err of Coef.		1.67E-005	
					para	Regression Output:		
					Constant			-0.002276
					Std Err of Y Est			0.0019856
					R Squared			0.9979925
					No. of Observations			9
					Degrees of Freedom			7
					X Coefficient(s)		2.53E-003	
					Std Err of Coef.		4.28E-005	
meta/para								
time in min	m	p			meta	Regression Output:		
0	0	0			Constant			-0.003608
5	0.0218146	0.0267469			Std Err of Y Est			0.0025442
10	0.0452234	0.0573952			R Squared			0.9991268
15	0.067972	0.0858175			No. of Observations			9
20	0.0935647	0.113663			Degrees of Freedom			7
25	0.1165388	0.1440197						
30	0.1422706	0.1817368			X Coefficient(s)		4.91E-003	
40	0.1917797	0.2409863			Std Err of Coef.		5.49E-005	
50	0.2459294	0.3083148						
		0.376752						
		0.4376454			para	Regression Output:		
					Constant			-0.004999
					Std Err of Y Est			0.0038833
					R Squared			0.9987131
					No. of Observations			9
					Degrees of Freedom			7
					X Coefficient(s)		6.17E-003	
					Std Err of Coef.		8.37E-005	

The rate constants for the deuterium reactions were calculated as shown below.

toluene/D2				Regression Output:		
			Constant			-0.032
time in min	1st order		Std Err of Y Est			0.0428952
0	0		R Squared			0.9932053
5	0.26		No. of Observations			4
10	0.6		Degrees of Freedom			2
15	0.98					
			X Coefficient(s)		6.56E-002	
			Std Err of Coef.		3.84E-003	

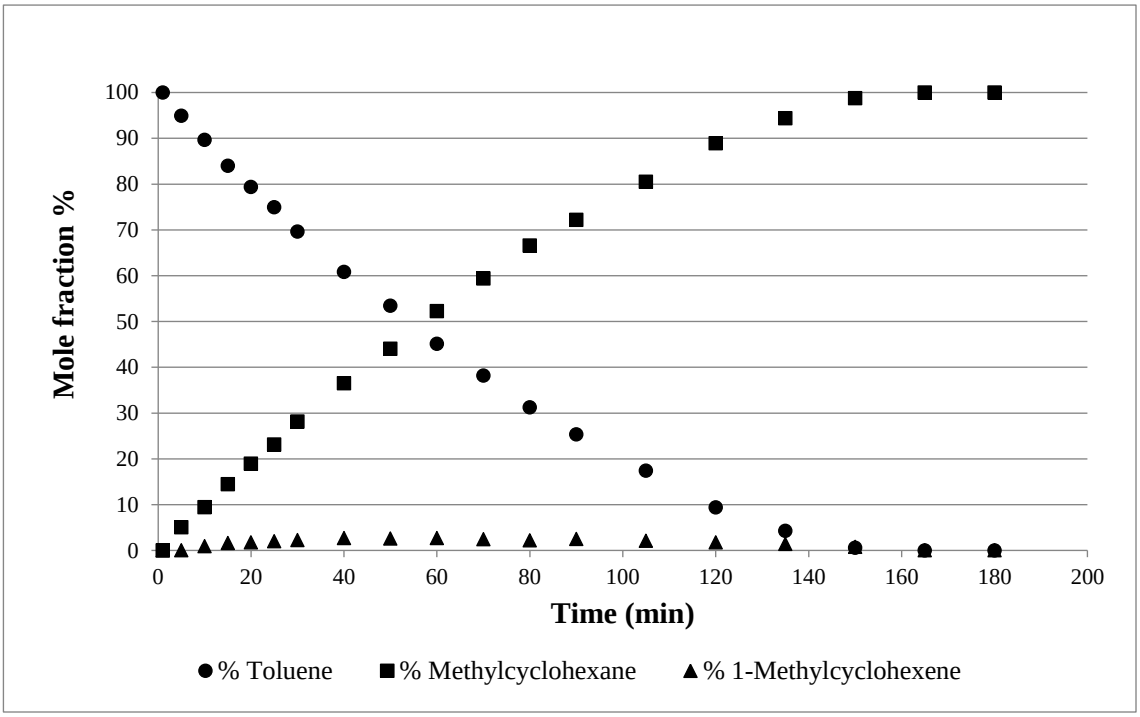
ethylbenzene/D2				Regression Output:		
			Constant			-0.028095
time in min	1st order		Std Err of Y Est			0.0281408
0	0		R Squared			0.9933611
5	0.13		No. of Observations			6
10	0.28		Degrees of Freedom			4
15	0.45					
20	0.61		X Coefficient(s)		3.29E-002	
25	0.83		Std Err of Coef.		1.35E-003	

propylbenzene/D2				Regression Output:		
			Constant			-0.006328
time in min	1st order		Std Err of Y Est			0.0057155
0	0		R Squared			0.9995203
5	0.06		No. of Observations			10
10	0.11		Degrees of Freedom			8
15	0.18					
20	0.25		X Coefficient(s)		1.25E-002	
25	0.3		Std Err of Coef.		9.70E-005	
30	0.37					
40	0.49					
50	0.62					
60	0.75					

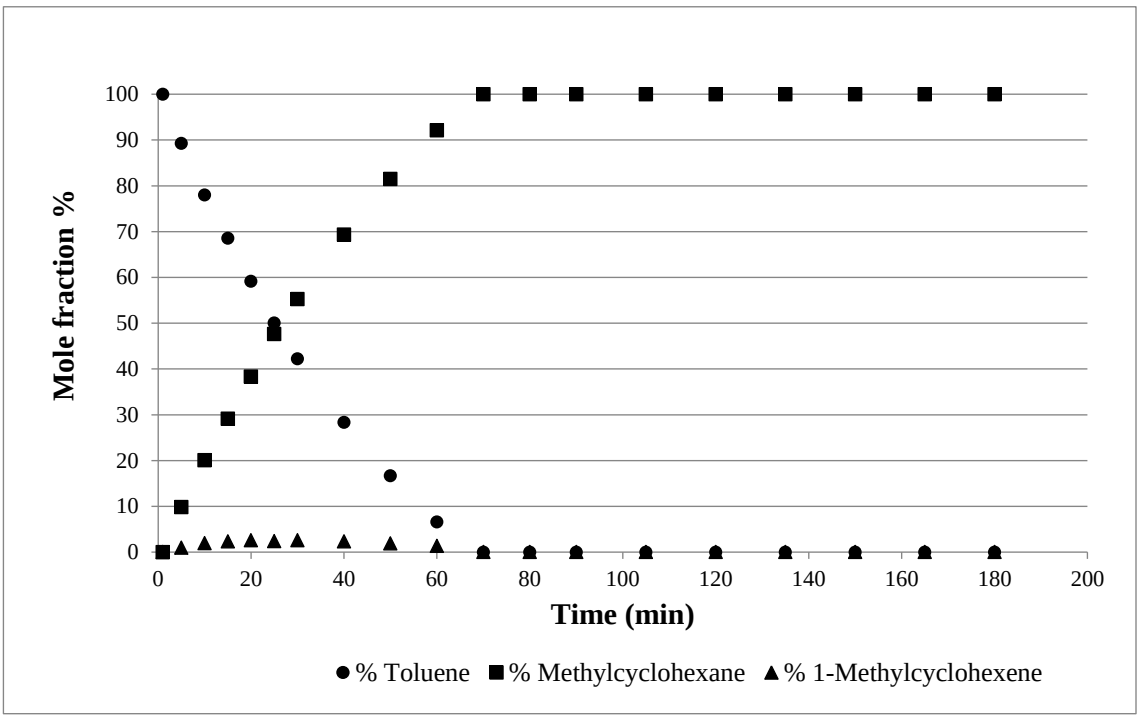
ortho/D2					Regression Output:		
				Constant			-0.010234
time in	mi	zero order (1	1st order	Std Err of Y Est			0.0105191
0		0	0	R Squared			0.9978069
5		8.5353096	0.0892172	No. of Observations			7
10		15.594755	0.1695407	Degrees of Freedom			5
15		23.277141	0.2649705				
20		30.263695	0.3604491	X Coefficient(s)		1.90E-002	
25		37.098351	0.4635978	Std Err of Coef.		3.98E-004	
30		43.545134	0.5717287				
meta/D2					Regression Output:		
				Constant			-0.009923
time in	mi	zero order (1	1st order	Std Err of Y Est			0.0117632
0		0	0	R Squared			0.9970304
5		9.8968761	0.104522	No. of Observations			5
10		19.313883	0.215272	Degrees of Freedom			3
15		28.546004	0.337232				
20		37.6399	0.4739306	X Coefficient(s)		2.36E-002	
				Std Err of Coef.		7.44E-004	
para/D2					Regression Output:		
				Constant			-0.022368
time in	mi	zero order (1	1st order	Std Err of Y Est			0.0363911
0		0	0	R Squared			0.9944765
5		23.617838	0.269421	No. of Observations			4
10		43.008064	0.5622604	Degrees of Freedom			2
15		60.616109	0.9318133				
				X Coefficient(s)		6.18E-002	
				Std Err of Coef.		3.25E-003	

The reaction order in hydrogen for toluene hydrogenation was determined as follows.

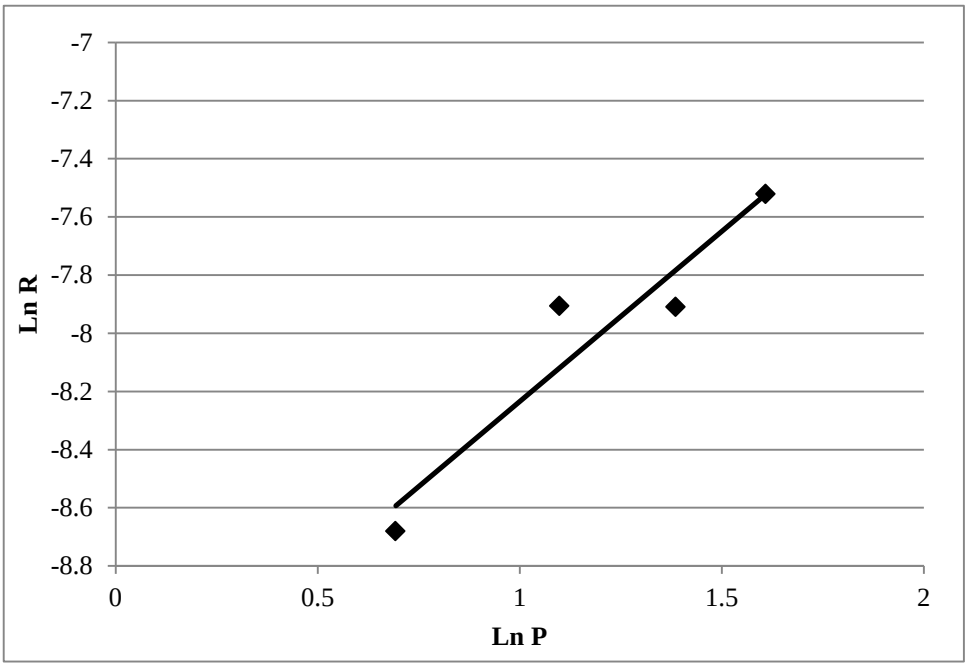
Toluene hydrogenation with 2 barg hydrogen at 323 K.



Toluene hydrogenation with 5barg hydrogen at 323 K.



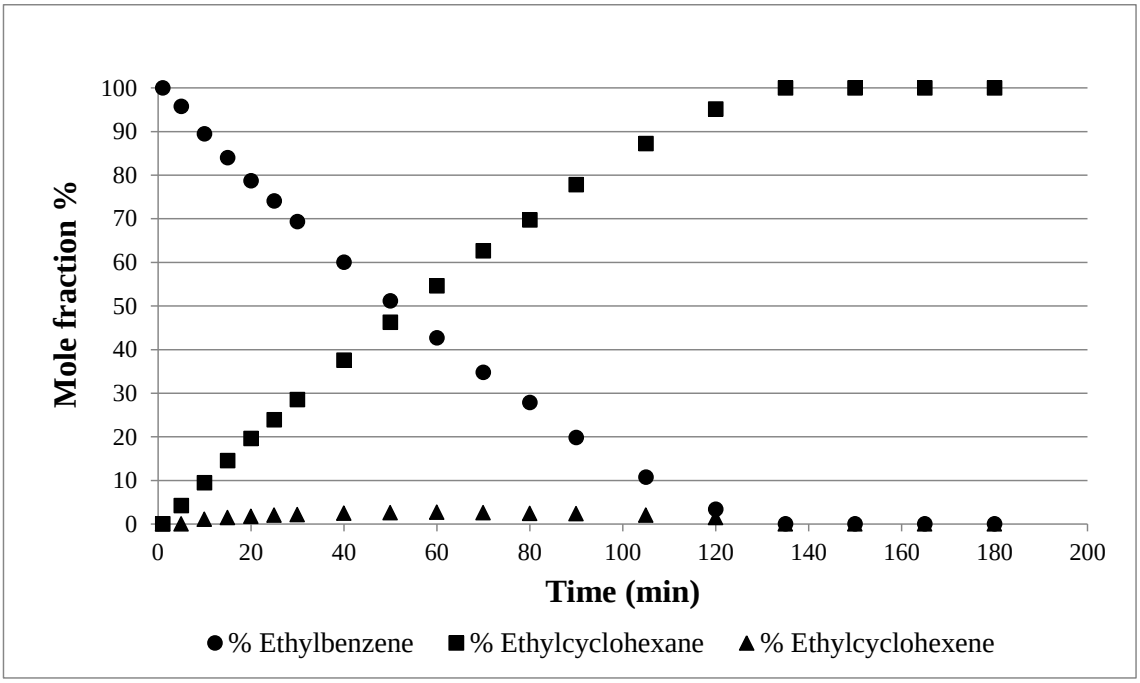
Determination of hydrogen order for toluene hydrogenation.



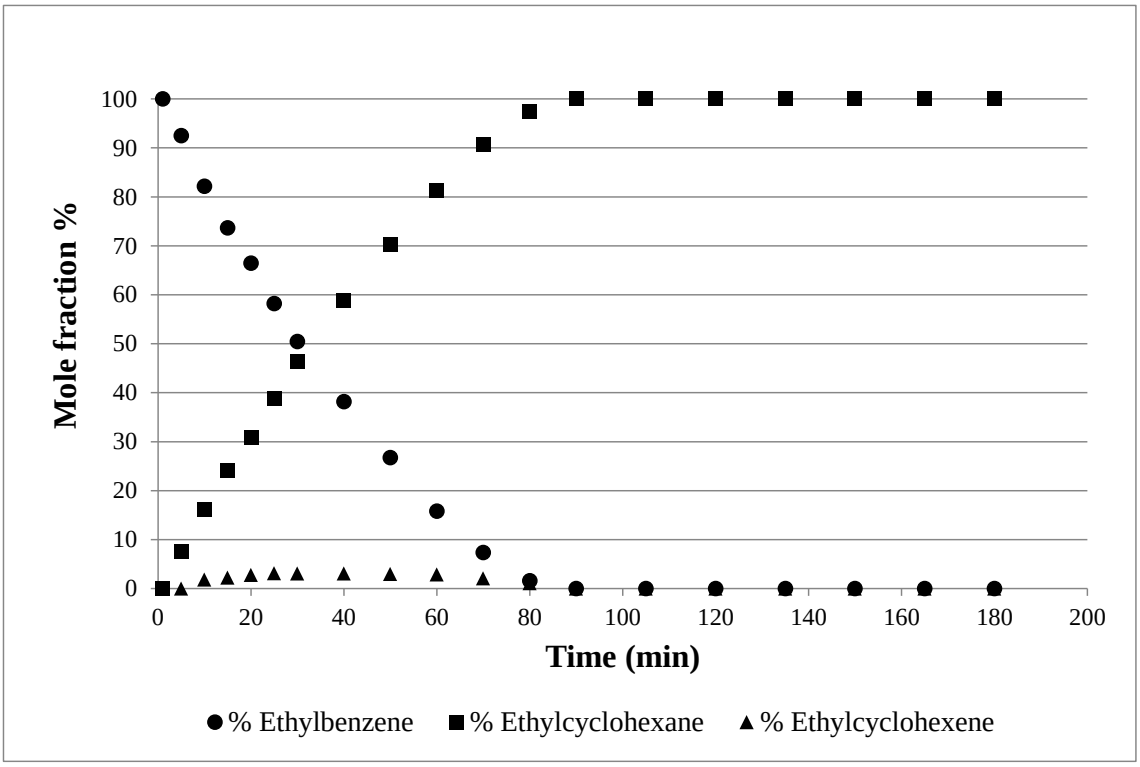
toluene						Regression Output:		
Pressure barg	ln(P)	ln(rate)			Constant			-9.402158
2	0.6931	-8.680185			Std Err of Y Est			0.1855074
3	1.0986	-7.906181			R Squared			0.9030078
4	1.3863	-7.908919			No. of Observations			4
5	1.6094	-7.520503			Degrees of Freedom			2
					X Coefficient(s)		1.1682427	
					Std Err of Coef.		0.2707327	

The reaction order in hydrogen for ethylbenzene hydrogenation was determined as follows.

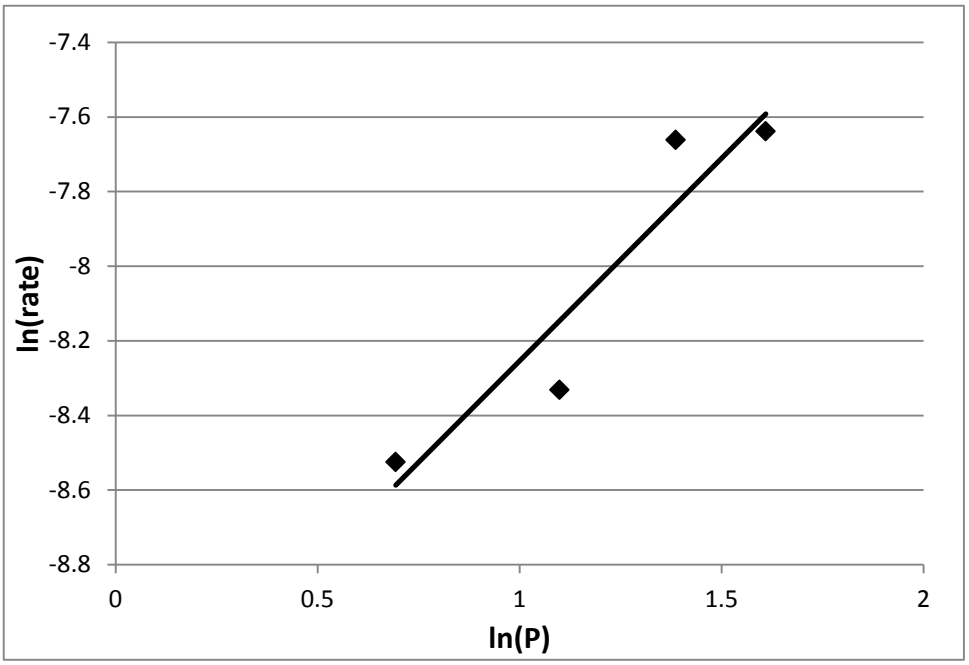
Ethylbenzene hydrogenation at 323 K and 2 barg hydrogen



Ethylbenzene hydrogenation at 323 K and 5 barg hydrogen



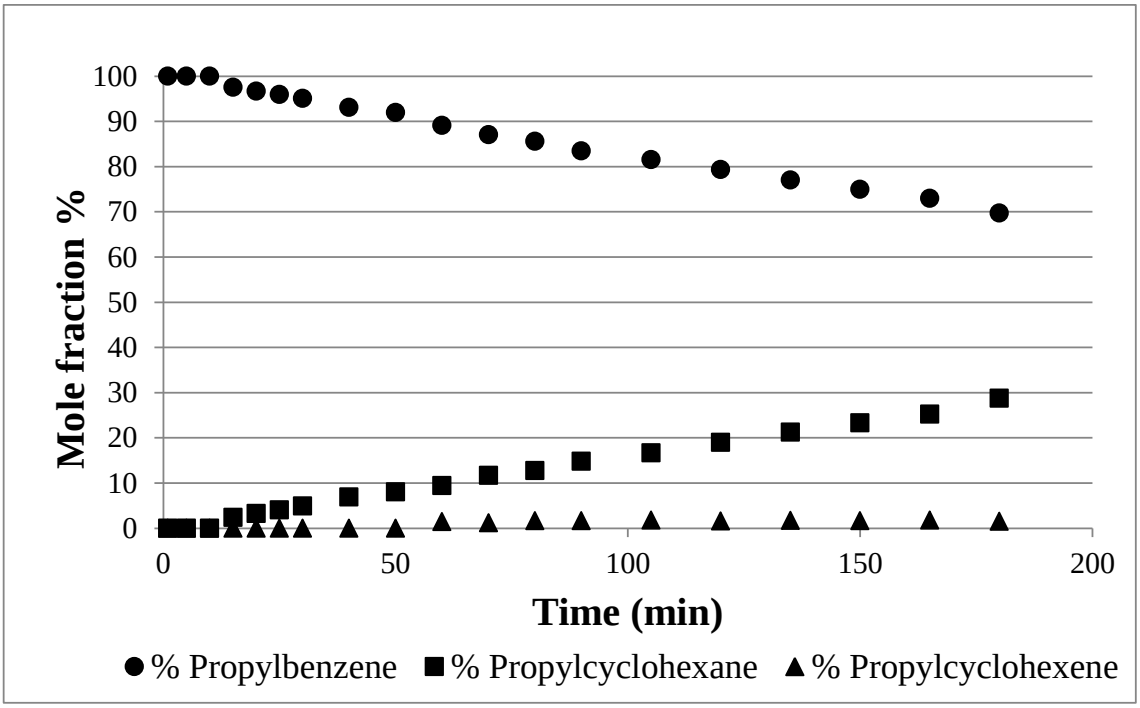
Determination of hydrogen order for ethylbenzene hydrogenation.



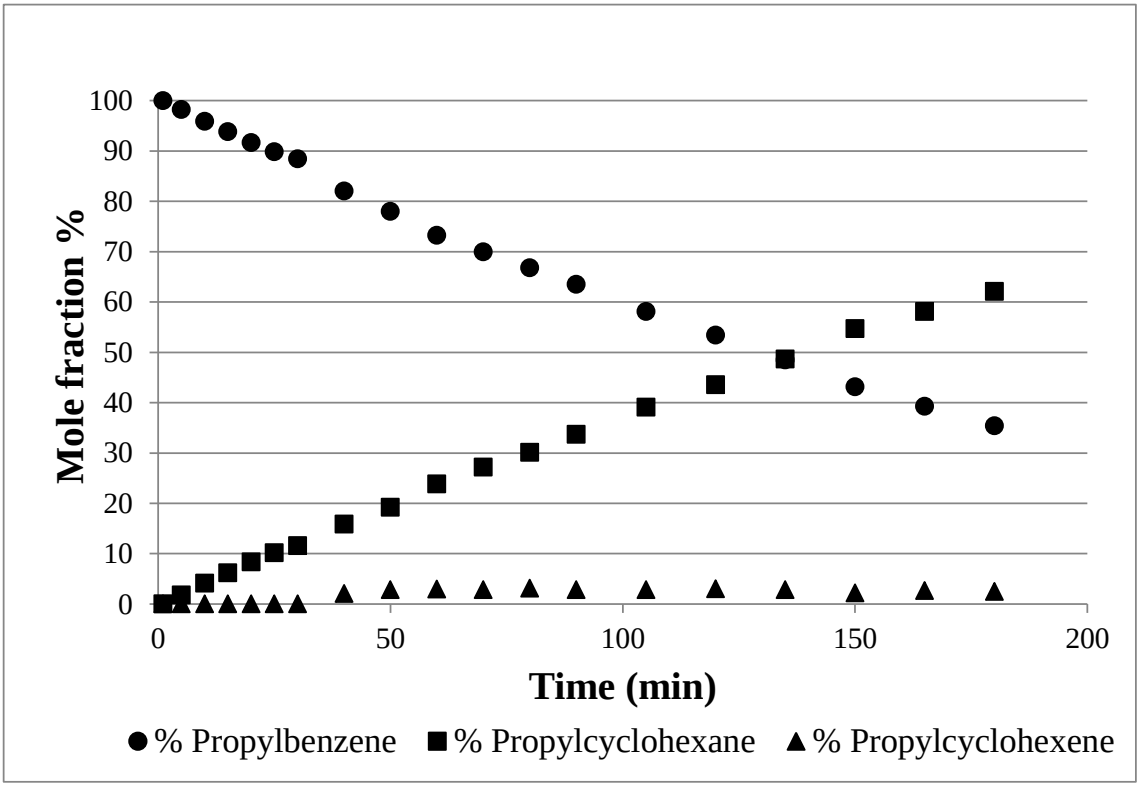
ethylbenzene						Regression Output:		
Pressure barg	ln(P)	ln(rate)			Constant			-9.339796
2	0.6931	-8.525262			Std Err of Y Est			0.187072
3	1.0986	-8.332335			R Squared			0.8878005
4	1.3863	-7.66262			No. of Observations			4
5	1.6094	-7.639423			Degrees of Freedom			2
					X Coefficient(s)		1.0860896	
					Std Err of Coef.		0.2730161	

The reaction order in hydrogen for propylbenzene hydrogenation was determined as follows.

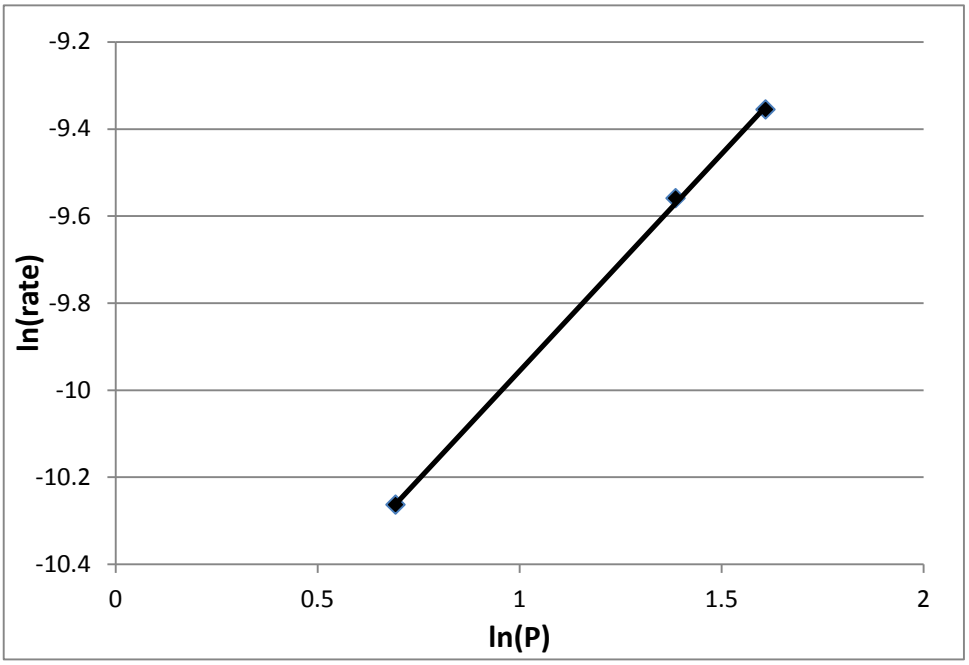
Propylbenzene hydrogenation at 323 K and 2 barg hydrogen



Propylbenzene hydrogenation at 323 K and 2 barg hydrogen



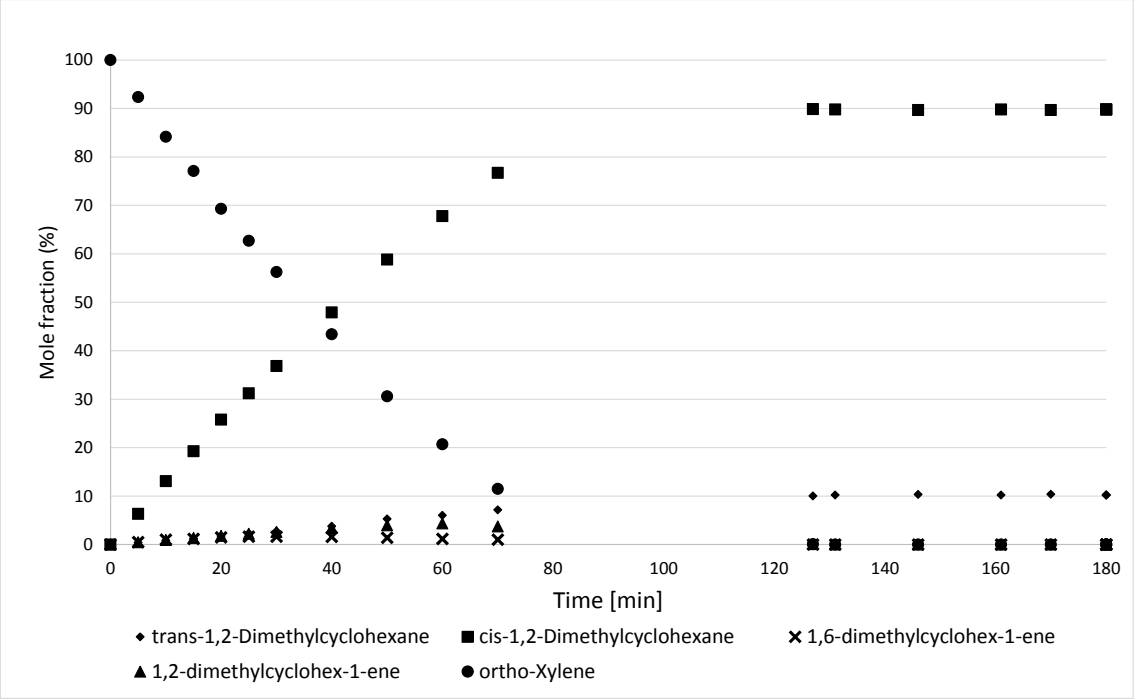
Determination of hydrogen order for propylbenzene hydrogenation.



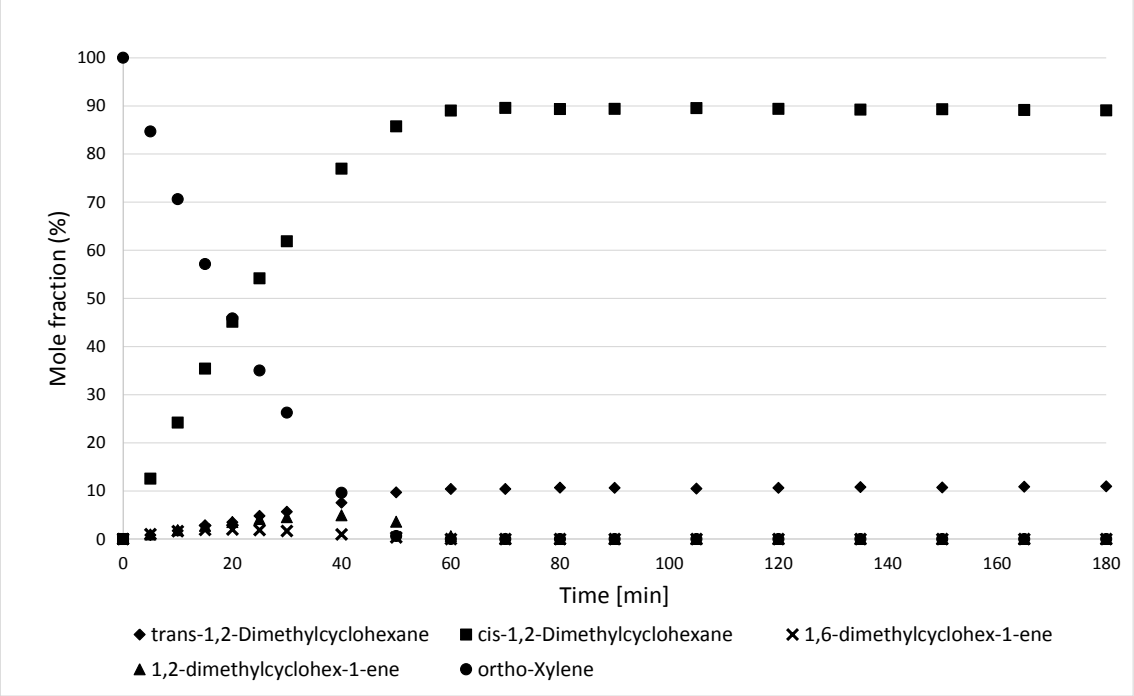
propylbenzene						Regression Output:		
Pressure barg	ln(P)	ln(rate)			Constant			-10.95253
2	0.6931	-10.26416			Std Err of Y Est			0.0139076
4	1.3863	-9.559503			R Squared			0.999574
5	1.6094	-9.356198			No. of Observations			3
					Degrees of Freedom			1
					X Coefficient(s)		0.996996	
					Std Err of Coef.		0.020581	

The reaction order in hydrogen for ortho-xylene hydrogenation was determined as follows.

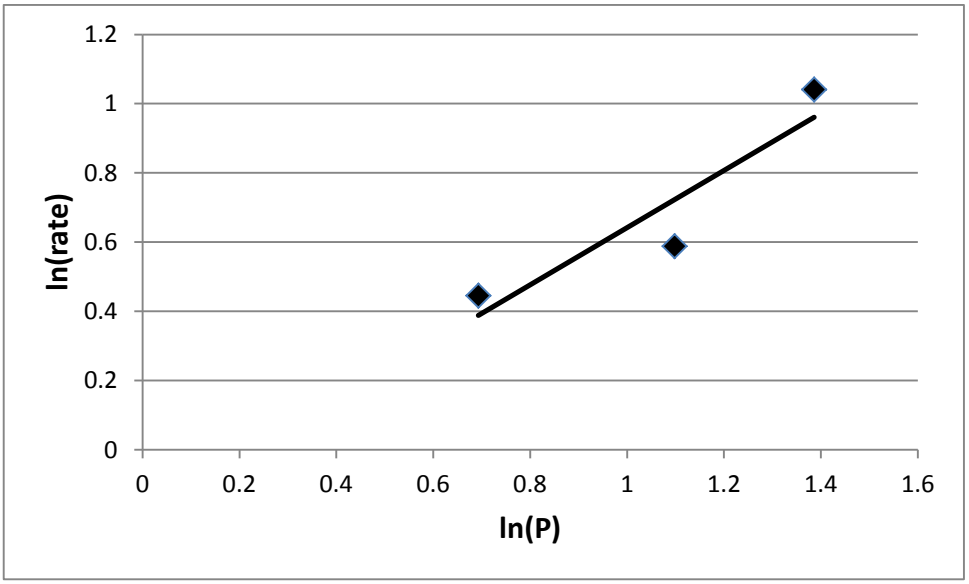
ortho-xylene hydrogenation at 323 K and 2 barg hydrogen.



ortho-xylene hydrogenation at 323 K and 4 barg hydrogen.



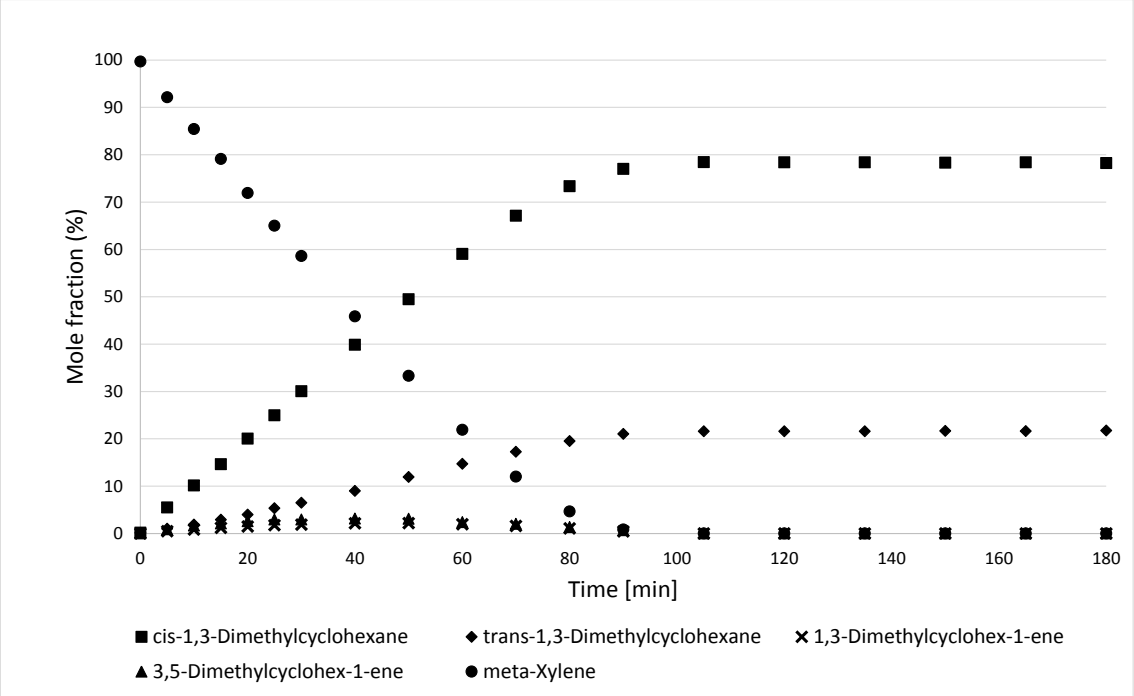
Determination of hydrogen order for ortho-xylene hydrogenation.



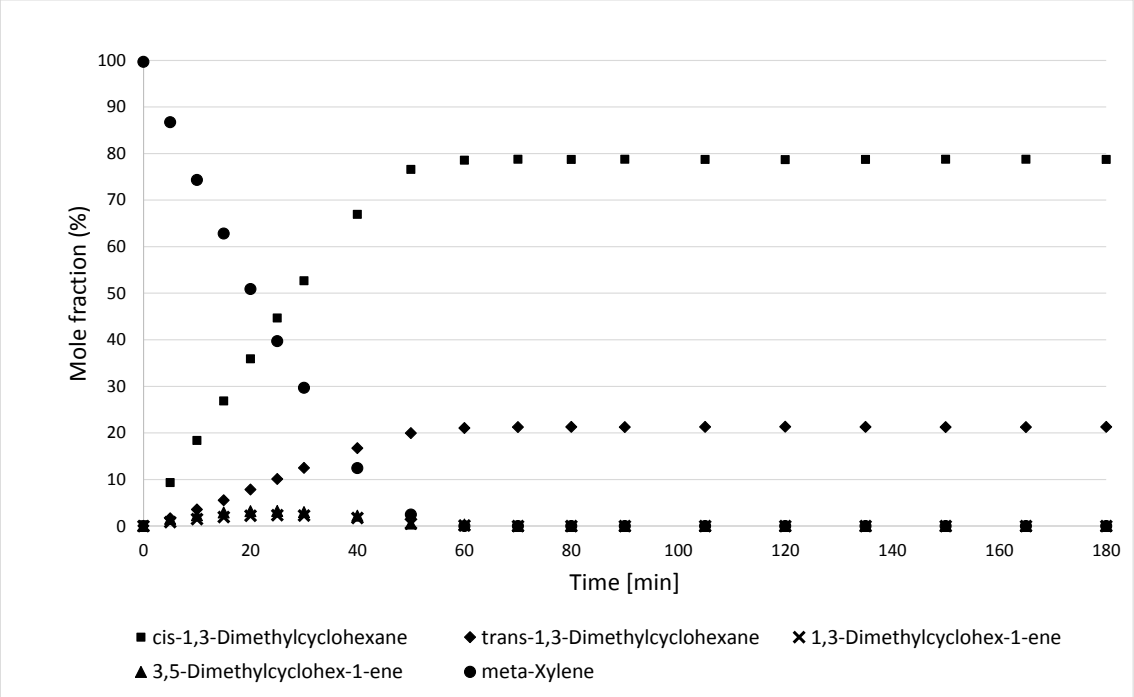
ortho-xylene					Regression Output:		
					Constant		-0.184132
order H2					Std Err of Y Est		0.1668237
Pressure barg	ln(P)	rate	ln(rate)		R Squared		0.8560394
2	0.693147	1.56	0.444686		No. of Observations		3
3	1.098612	1.8	0.587787		Degrees of Freedom		1
4	1.386294	2.83	1.040277				
					X Coefficient(s)	0.8260238	
					Std Err of Coef.	0.3387407	

The reaction order in hydrogen for meta-xylene hydrogenation was determined as follows.

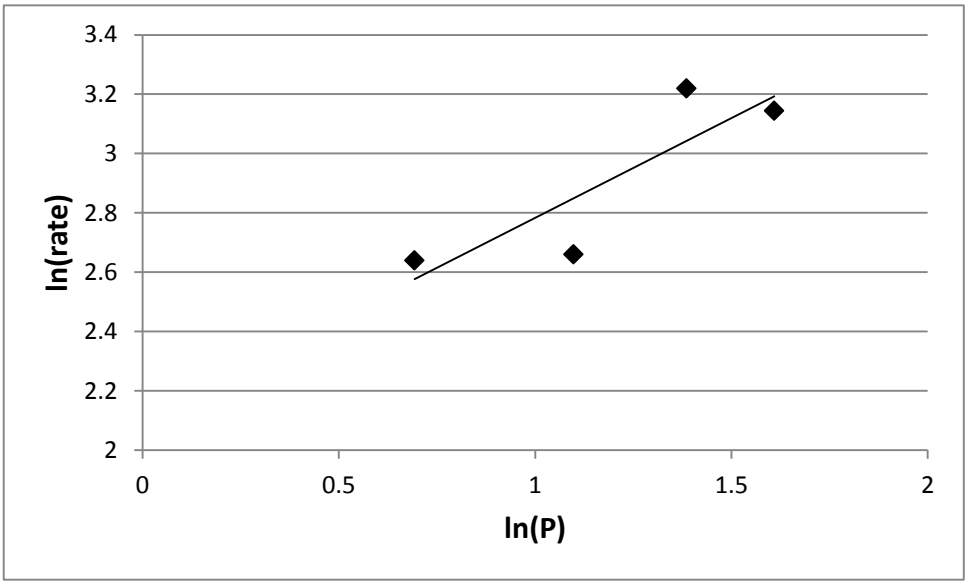
meta-xylene hydrogenation at 323 K and 2 barg hydrogen.



meta-xylene hydrogenation at 323 K and 4 barg hydrogen.



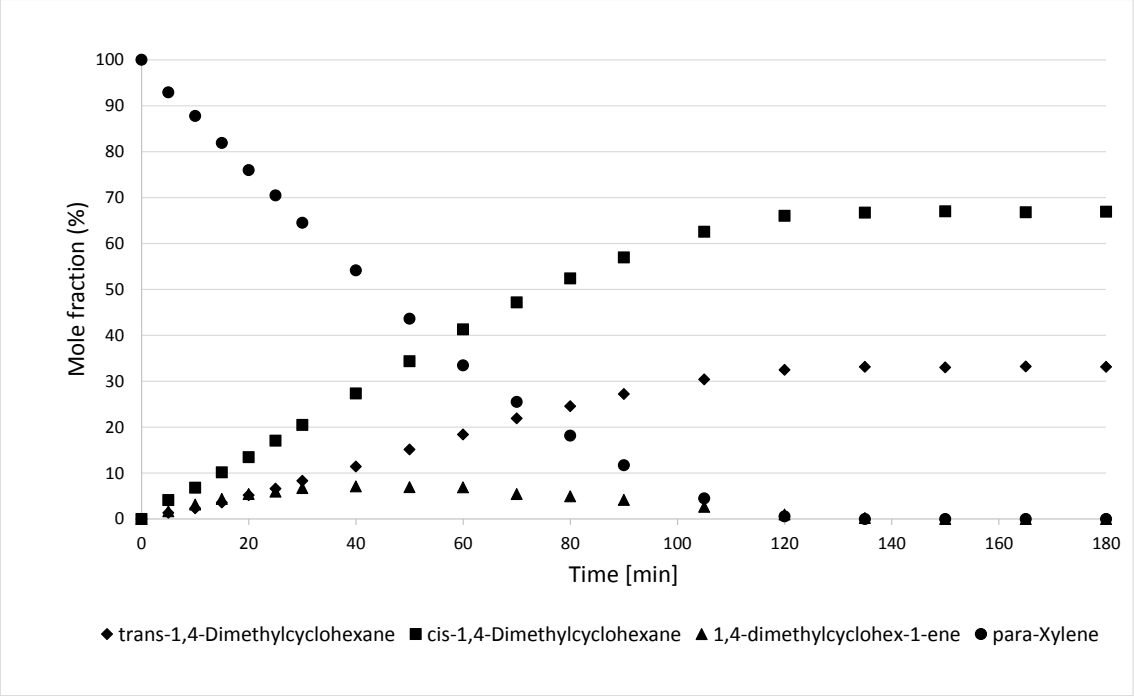
Determination of hydrogen order for meta-xylene hydrogenation.



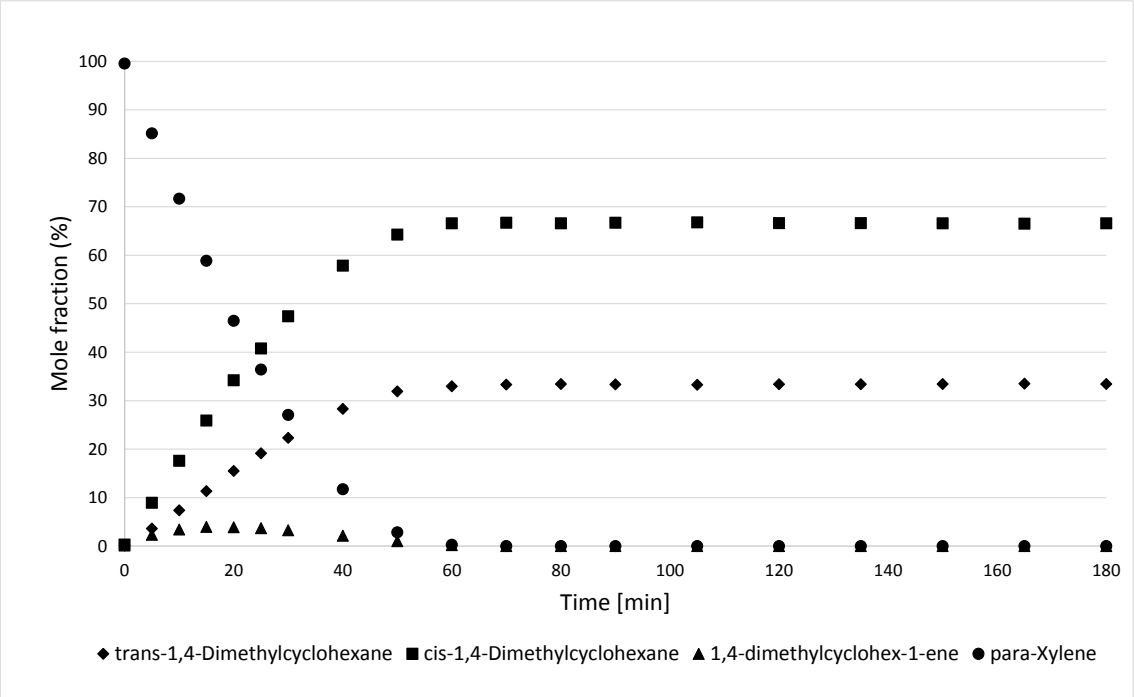
meta-xylene							
					Regression Output:		
					Constant		2.1096635
order H2					Std Err of Y Est		0.1910728
Pressure barg	ln(P)	rate	ln(rate)		R Squared		0.7445925
2	0.693147	14	2.639057		No. of Observations		4
3	1.098612	14.3	2.66026		Degrees of Freedom		2
4	1.386294	25	3.218876				
5	1.609438	23.2	3.144152		X Coefficient(s)	0.6733571	
					Std Err of Coef.	0.2788611	

The reaction order in hydrogen for para-xylene hydrogenation was determined as follows.

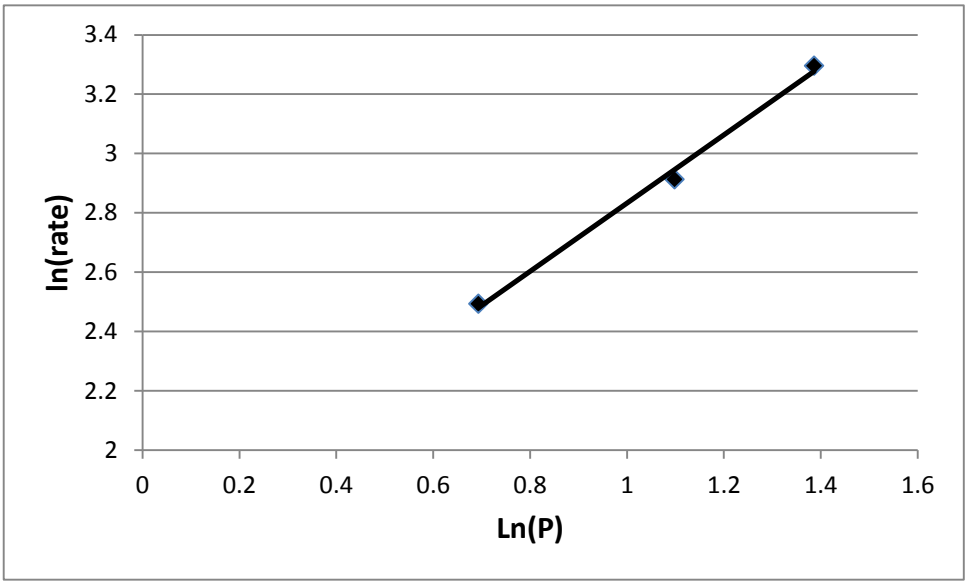
para-xylene hydrogenation at 323 K and 2 barg hydrogen.



para-xylene hydrogenation at 323 K and 4 barg hydrogen.



Determination of hydrogen order for para-xylene hydrogenation.



para-xylene							
					Regression Output:		
					Constant		1.6824216
order H2					Std Err of Y Est		0.0409252
Pressure barg	ln(P)	rate	ln(rate)		R Squared		0.9948037
2	0.693147	12.1	2.493205		No. of Observations		3
3	1.098612	18.4	2.912351		Degrees of Freedom		1
4	1.386294	27	3.295837				
					X Coefficient(s)	1.1498009	
					Std Err of Coef.	0.0831	

Determination of orders of reaction in the aromatic species. A relative concentration of 1 represents the standard concentration of ~8 mmol. All reactions performed at 323 K and 3 barg hydrogen.

toluene						Regression Output:		
relative conc	ln(conc)	ln(rate)			Constant			-7.675855
1	0	-7.93515			Std Err of Y Est			0.2361348
0.5	-0.693147	-7.816			R Squared			0.1437351
0.75	-0.287682	-7.53825			No. of Observations			4
1.5	0.4054651	-7.51205			Degrees of Freedom			2
					X Coefficient(s)		0.1703811	
					Std Err of Coef.		0.2940553	
ethylbenzene						Regression Output:		
relative conc	ln(conc)	ln(rate)			Constant			-8.314054
1	0	-8.33204			Std Err of Y Est			0.037839
0.5	-0.693147	-8.08663			R Squared			0.9531388
0.75	-0.287682	-8.18362			No. of Observations			3
					Degrees of Freedom			1
					X Coefficient(s)		-0.346514	
					Std Err of Coef.		0.0768333	
propylbenzene						Regression Output:		
relative conc	ln(conc)	ln(rate)			Constant			-9.697666
0.5	-0.693147	-9.09439			Std Err of Y Est			0.0358447
0.75	-0.287682	-9.4838			R Squared			0.9970865
1.5	0.4054651	-10.0292			No. of Observations			3
					Degrees of Freedom			1
					X Coefficient(s)		-0.844003	
					Std Err of Coef.		0.0456234	

meta-xylene						Regression Output:		
					Constant			2.8559317
Relative conc	ln(conc)	rate	ln(rate)		Std Err of Y Est			0.1667831
0.5	-0.69315	35.7	3.575151		R Squared			0.937949
0.75	-0.28768	22.8	3.126761		No. of Observations			4
1	0	14.3	2.66026		Degrees of Freedom			2
2	0.693147	10.2	2.322388					
					X Coefficient(s)		-0.906669	
					Std Err of Coef.		0.1648992	
para-xylene						Regression Output:		
					Constant			2.9985652
Relative conc	ln(conc)	rate	ln(rate)		Std Err of Y Est			0.1013951
0.5	-0.69315	33.8	3.520461		R Squared			0.9525333
0.75	-0.28768	22.8	3.126761		No. of Observations			4
1	0	18.4	2.912351		Degrees of Freedom			2
2	0.693147	13.7	2.617396					
					X Coefficient(s)		-0.635103	
					Std Err of Coef.		0.1002498	
ortho-xylene						Regression Output:		
					Constant			2.2870995
Relative conc	ln(conc)	rate	ln(rate)		Std Err of Y Est			0.032343
0.5	-0.69315	15.8	2.76001		R Squared			0.9953839
0.75	-0.28768	11.5	2.442347		No. of Observations			4
1	0	10.1	2.312535		Degrees of Freedom			2
2	0.693147	6.2	1.824549					
					X Coefficient(s)		-0.664075	
					Std Err of Coef.		0.0319777	